Cu(II), Pb(II) and Cd(II) complex formation with pyridine-2,6-dicarboxylate and 4-hydroxypyridine-2,6-dicarboxylate in aqueous solutions

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Interactions between pyridine-2,6-dicarboxylic acid and 4-hydroxypyridine-2,6-dicarboxylic acid with Cu(II), Pb(II) and Cd(II) ions were characterized in aqueous solutions (20 °C; I = 0.4 (KNO$_3$)) by means of d.c.-polarography. In solutions with excess of ligand Cu(II), Pb(II) and Cd(II) form 1:2 complexes with the tridentate dianion of pyridine-2,6-dicarboxylic acid (dipic^{2-}) from weak acid to alkaline solutions. The values of logβ_2 for Cu(II), Pb(II) and Cd(II) are 16.1, 11.8 and 11.0, respectively. The complexing ability of pyridine-2,6-dicarboxylic acid is higher in acid solutions and lower in alkaline solutions than that of 4-hydroxypyridine-2,6-dicarboxylic acid. This difference is attributed to the OH-group, which can deprotonate in basic pH. In acid solutions the OH-group acts as an electron acceptor and reduces the electron donation available to the nitrogen atom in 4-hydroxypyridine-2,6-dicarboxylic acid, whereas in alkaline solution the OH-group is deprotonated, and the deprotonated O$^-$ group acts as an electron donor and increases the coordination ability of the ligand. The triple-deprotonated anion of 4-hydroxypyridine-2,6-dicarboxylic acid (chel^{3-}) forms a stable diligand complex with Cu(II), the stability constant logarithm being 21.5 ± 0.2.

Key words: copper(II), lead(II), cadmium(II), pyridine-2,6-dicarboxylic acid, 4-hydroxypyridine-2,6-dicarboxylic acid, complex formation

INTRODUCTION

Many transition and heavy metal cations play an active role in a great number of various biological processes, being a component of several vitamins and drugs. Pyridinedicarboxylic acids and their derivatives belong to an interesting series of compounds with biological applications [1]. Pyridine-2,6-dicarboxylic acid (dipicolinic acid) is present in nature as an oxidative degradation product of vitamins, coenzymes and alkaloids and is a component of fulvic acids. It has frequently been cited in the literature as a plant sterilizing and water germicidal agent and an antioxidant for ascorbic acids in foods [2]. Pyridine-2,6-dicarboxylic acid is almost unique to bacterial spores and may constitute as much as 15% of their weight [3]. Pyridine-2,6-dicarboxylic acid is a desirable metal ion ligand because of its low toxicity and amphophilic nature. Pyridine-3-carboxylic acid (commonly known as niacin or vitamin B$_3$), which is closely related to pyridine-2,6-dicarboxylic acid, is the precursor of the coenzyme NAD and is required in the human diet. Pyridine-2,6-dicarboxylic acid is furthermore related to pyridine-2,3-dicarboxylic acid (quinolinic acid), which is also an intermediate in the tryptophan degradation pathway and a precursor of NAD [4].

The interaction of transition and heavy metal ions with naturally occurring ligands in living organisms such as pyridine-2,6-dicarboxylic acid (H$_2$dipic) or its isomer 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid) (H$_3$chel) is important for evaluating the potential beneficial and deteriorative effects of these ions.

Most studies have focused on to synthesis and structural investigations of metal H$_2$dipic complexes in solid state. Much is known on the preparation, crystalline structure and properties of the Cu(II) [5–8], Fe(II) [9], Fe(III) [9–12], Mn(II) [6, 13], Mn(III)[14, 15], Ag(I) [1, 16], Co(II) [5, 6], Co(III) [17], Pt(II) [18], Ti(III) [19], Ni(II) [5, 6] and Zn(II) [5, 6] complexes. The metal-to-ligand stoichiometry 1:1 was found for complexes of Cu(II) [8], Fe(II) [9], dinuclear and polymeric complexes where deter-

mined in the case of Ag(I) complexes [1, 16], whereas 1:2 complexes were observed for Cu(II) [5–7], Fe(II) and Fe(III) [9–12], Mn(II) and Mn(III) [6, 13–15], Co(II) and Co(III) [5, 6, 17], Pt(II) [18], Ti(III) [19], Ni(II) [5, 6] and Zn(II) [5, 6].

Most of the complexes listed above contain double deprotonated anion $dipic^{2-}$, whereas monodeprotonated $Hdipic^-$ forms complexes with Co(II), Ni(II), Cu(II), Zn(II) [5] and Mn(II) [5, 13]. In addition, a Cu(II) complex containing one unit of protonated H_2Dipic and one unit of double deprotonated $dipic^{2-}$ was synthesized [7].

Data on the synthesis of metal ion complexes with 4-hydroxypyridine-2,6-dicarboxylic acid (H_3chel) are not numerous. The metal-to-ligand stoichiometry 1:3 was found for a complex of Cr(III) containing monodeprotonated anions of H_2chel^- [20].

Solution chemistry of H_2dipic has been investigated. The UV-visible and IR absorption and ^{13}C NMR spectra of pyridine-2,6-dicarboxylic acid and of all other possible isomers of pyridinedicarboxylic acid were determined [21]. The pK_a values for H_2dipic had previously been reported [22] and the average values equal to 2.2 and 4.6 were obtained for pK_{a1} and pK_{a2}, respectively, documenting that in neutral and alkaline solutions H_2dipic exists as dianion $dipic^{2-}$. Investigations on the electrochemical behaviour of pyridine-2,6-dicarboxylic acid on HMDE showed that H_2dipic is strongly adsorbed on a mercury electrode only in acidic solutions, *i. e.* double deprotonated anion $dipic^{2-}$ does not adsorb on Hg [23].

Data on the aqueous solution speciation of metal ion complexes with double deprotonated pyridine-2,6-dicarboxylic acid ($dipic^{2-}$) are listed in Table 1. One can see that most heavy metal ions form complexes with metal-to-ligand stoichiometry 1:1 as well as 1:2. The complexes formed are of medium stability, except with Hg(II), which forms a relatively stable complex, with the stability constant logarithm being over 20 (Table 1).

Interaction of 4-hydroxypyridine-2,6-dicarboxylic acid with metal ions in aqueous solutions is less investigated (Table 2). Comparison of the stability constants obtained with those of metal ion complexes with pyridine-2,6-dicarboxylic acid shows that in general 4-hydroxypyridine-2,6-dicarboxylic acid forms more stable complexes with heavy metal ions than pyridine-2,6-dicarboxylic acid (*cf.* Tables 1 and 2). It can be mentioned that 4-hydroxypyridine-2,6-dicarboxylic acid has stronger acidic properties in comparison with pyridine-2,6-dicarboxylic acid, *i. e.* pK_{a1} and pK_{a2} values of the carboxylic groups are 1.4 and 3.1, respectively [22]. In addition, at higher pH values the ionization of OH-group of 4-hydroxypyridine-2,6-dicarboxylic acid occurs, the pK_{a3} value being 10.9 [22].

Table 1. **Stability constants of heavy metal ion complexes with pyridine-2,6-dicarboxylate ($dipic^{2-}$) in aqueous solutions**

Metal ion	$log\beta_1$	$log\beta_2$	Reference
Cu(II)	10.0	16.3	[24]
	9.14	16.52	[25]
	9.14	16.51	[26]
	8.9	17.1	[27]
	8.88	16.17	[28]
		16.4	[29]
Pb(II)	5.1	8.2	[30]
	8.70	11.60	[25]
	8.66	11.55	[31]
	8.69	11.57	[32]
Cd(II)	5.7	10.0	[30]
	6.75	11.11	[25]
	6.51	10.77	[33]
Fe(II)	5.71	10.36	[25]
Fe(III)	10.91	17.13	[34]
		16.74	[35]
Co(II)	7.0	12.5	[24]
	6.65	12.70	[25]
Ni(II)	8.0	14.1	[24]
	6.95	13.50	[25]
Zn(II)	7.0	13.0	[24]
	6.35	11.88	[25]
Mn(II)	5.01	8.49	[25]
Hg(II)		20.28	[25]
Pd(II)	16.0		[36]
VO_2^+	15.79		[37]

Table 2. **Stability constants of metal ion complexes with 4-hydroxypyridine-2,6-dicarboxylate ($chel^{3-}$) in aqueous solutions**

Metal ion	$log\beta_1$	$log\beta_2$	Reference
Cu(II)	12.2	22.1	[38]
Co(II)	8.4	16.2	[38]
Mn(II)	6.7		[38]
Ni(II)	9.2	17.3	[38]
Zn(II)	9.3	17.8	[38]
Ba(II)	3.98		[39]
Ca(II)	5.40		[39]
Mg(II)	3.68		[39]
Sr(II)	4.34		[39]

Given the recent results showing that some transition metal complexes with pyridine-2,6-dicarboxylic acid have beneficial effects in normalizing elevated blood glucose levels in diabetic rats [40, 41], fundamental information on solution chemistry of metal complexes with pyridinedicarboxylic acid ligands is important. The present study was carried out to specify equilibria in solutions of pyridine-2,6-dicarboxylic and 4-hydroxypyridine-2,6-dicarboxylic acids in the presence of the divalent metal ions Cu(II), Pb(II) and Cd(II) in a wide pH range, and to compare the

results with those obtained earlier for an isomer of pyridine-2,6-dicarboxylic acid, *i. e.* pyridine-2,5-dicarboxylic acid [42]. One of the other aims of the work presented herein was to determine the complexation level (*i. e.* the concentration of free (uncomplexed) metal ions) of metal ions mentioned in the presence of pyridinecarboxylic acids.

EXPERIMENTAL

Reagents

Pyridine-2,6-dicarboxylic acid (H$_2$dipic) was from Aldrich, and 4-hydroxypyridine-2,6-dicarboxylic acid (H$_3$chel) was from TCI (Japan). Unless otherwise specified, analytical grade reagents were used. KNO$_3$ and KOH solutions were used to keep the ionic strength (*I*) of the solutions constant and equal to 0.4 M. The solutions were prepared in triple distilled water.

Apparatus

Polarographic curves were recorded with a PU-1 polarograph using a dropping mercury electrode in a thermostated three-electrode cell at 20 ± 0.1 °C. The potential scanning rate was 100 mV min^{-1}. The capillary characteristics of the dropping mercury electrode (DME) were as follows: m = 2.95 mg/s, t = = 3.73 s. The reference electrode was an Ag/AgCl electrode filled with saturated KCl. The solutions were deaerated by bubbling Ar through the solution before use.

The visible spectra were recorded with a Perkin Elmer Lambda 35 UV/VIS spectrometer at 20 ± 1 °C in 1.0 cm path length quartz cells. The optical blank solution was pure water.

Procedures

The values of the actual half-wave potential $E_{1/2}$ were determined from a plot of $\log(\bar{i}/\bar{i}_{\lim} - \bar{i})$ against E. The values of the transition coefficient α and the reversible half-wave potential $-E_{1/2}^r$ were calculated using equations (1) and (2) [43], where $E_{1/2}'$ is the half-wave potential determined by extrapolation of the linear part of the graph $\log(\bar{i}/\bar{i}_{\lim} - \bar{i})$ against E at sufficiently negative potentials, and $E_{1/11}$ is the potential where the current exceeds the value equal to 1/11 of the limiting current value. The diffusion coefficient values (*D*) were calculated using the Ilkovic equation (3) [44], where $\bar{i}_{dif}$ is the limiting diffusion current (μA), n is the number of electrons involved in electrochemical reaction, c is the total concentration of Cu(II) ions (mM), m is the flow

rate of Hg (mg/s), and t is the time of the drop formation (s). The corrections for a decrease in $\bar{i}_{\lim}$ were made in calculation of $\Delta E_{1/2}^r$ for the case of complex formation as shown in equation (4) [44].

$$\alpha = 2.303 \frac{RT}{nF} \left\{ \frac{\Delta \log(\bar{i}/\bar{i}_{\lim} - \bar{i})}{\Delta(-E)} \right\}_{E \to -\infty}, \quad (1)$$

$$E_{1/2}^r = E_{1/11} - 2.303 \frac{RT}{nF} \left\{ \log \left[10 - \right. \right.$$

$$\left. \left. - \exp \frac{\alpha nF}{RT}(E_{1/11} - E_{1/2}') \right] \right\}, \quad (2)$$

$$D^{1/2} = \frac{\bar{i}_{dif}}{607ncm^{2/3}t^{1/6}}, \quad (3)$$

$$\Delta E_{1/2}^r = (E_{1/2}^r)_{compl} - (\Delta E_{1/2}^r)_{free} -$$

$$- 2.303 \frac{RT}{nF} \log \sqrt{\frac{\bar{i}_{\lim \, free}}{\bar{i}_{\lim \, compl}}}. \quad (4)$$

The concentrations of free (uncomplexed) M^{2+} ions were calculated from $\Delta E_{1/2}^r$ as shown in equation (5), where [M(II)]$_0$ is the total M^{2+} concentration. The stability constants (β) of Me(II) complexes with pyridinedicarboxylic acids were obtained during iterative approximation by minimizing the least-squares functional obtained from equation (6), where [L] is an equilibrium concentration of the ligand form taking part in complex formation (M), and a is an activity of OH$^-$ ions. The stability constants were calculated assuming that the determination of the reversible half-wave potential was within ± 2 mV. The accuracy of the stability constants can be calculated using the ± 2 mV limit. The species were fit to the polarographic data, but if the calculation diverges to infinity, the species was not considered further.

$$pM = nF/2.303RT(-\Delta E_{1/2}^r) - \log[M(II)]_0, \quad (5)$$

$$\sum_{x_i=0}^{N} \beta_{x_i} \left[L^{n-} \right]^{x_i} = \exp \left[(nF/RT)\left(-\Delta E_{1/2}^r \right) \right] - 1. \quad (6)$$

The molar extinction coefficient values of the individual complexes were calculated at λ_{max} according to equation (7), where c is the concentration (M) of the complexes, $A_{\lambda max}$ is the light absorbance at wavelength λ_{max}, and l is the cell width (cm).

$$\varepsilon_{\lambda max} = A_{\lambda max} / cl. \quad (7)$$

RESULTS AND DISCUSSION

Metal ion complexes with pyridine-2,6-dicarboxylic acid

The quasi-reversible, diffusion-controlled (limiting current temperature coefficient values are in the range 1.1–1.4%/deg, and the dependencies of the limiting current on the square root of the mercury column height are linear) polarographic waves of Cu(II), Pb(II) and Cd(II) reduction in the presence of pyridine-2,6-dicarboxylic acid are observed in a wide pH range from 1.5 to 12.0 (Table 3) and allow calculations of

the reversible half-wave potential $E_{1/2}^{r}$ and, subsequently, the equilibrium characteristics of the systems under investigation.

Cu(II)–*pyridine-2,6-dicarboxylic acid*

The actual half-wave potential $E_{1/2}$ of the polarographic waves of Cu(II) reduction shifts to more negative potentials with the increase in pH from 1.5 up to 6. The $E_{1/2}$ as well as $E_{1/2}^{r}$ remains practically constant with a further increase in alkalinity up to pH 12.0 (Table 3).

Table 3. **Characteristics of the process of metal ion reduction on a DME in solutions of pyridine-2,6-dicarboxylic acid ([M(II)]$_0$ = 5 mM; [H$_2$dipic]$_0$ = 50 mM; 20 °C; I = 0.4)**

Metal ion	pH	$-E_{1/2}$, mV	$-E_{1/2}^{'}$, mV	$-E_{1/11}$, mV	α	$-E_{1/2}^{r}$, mV	$-\Delta E_{1/2}^{r}$, mV
Cu(II)	1.5	63	48	33	0.66	59	124
	1.8	95	93	65	0.88	79	144
	2.1	120	116	90	0.88	107	172
	2.4	148	141	117	0.81	138	203
	2.7	166	162	136	0.83	155	220
	3.0	190	182	155	0.67	177	243
	3.3	212	204	175	0.62	197	262
	3.6	242	236	204	0.66	223	288
	5.0	273	269	239	0.76	256	231
	6.0	276	272	246	0.67	269	327
	8.0	276	271	247	0.70	270	328
	10.0	275	272	246	0.68	268	327
	12.0	277	270	245	0.66	267	326
Pb(II)	1.5	407	400	377	0.76	399	59
	2.0	434	426	406	0.81	429	88
	3.0	479	472	448	0.76	470	128
	4.0	518	513	482	0.69	501	159
	5.0	538	517	508	0.68	535	194
	6.0	547	544	515	0.85	545	204
	7.0	546	542	516	0.80	544	204
	8.0	548	543	514	0.88	546	205
	10.0	547	544	515	0.76	544	204
	11.0	567	551	536	0.54	562	221
	12.0	591	568	560	0.35	587	247
	13.0	641	634	612	0.48	638	296
Cd(II)	1.5	562	556	532	0.81	553	19
	1.8	568	563	537	0.76	558	24
	2.1	584	581	553	0.88	567	34
	2.4	595	591	566	0.88	584	51
	2.7	609	604	577	0.74	598	64
	3.0	627	621	594	0.73	615	82
	3.3	638	634	603	0.73	620	87
	3.6	665	659	627	0.64	647	113
	4.2	696	690	659	0.66	679	145
	4.5	703	698	667	0.67	687	153
	4.8	713	705	677	0.67	699	165
	5.1	719	713	682	0.60	704	170
	6.0	725	715	690	0.56	714	180
	8.0	726	714	691	0.60	713	179
	10.0	724	715	690	0.58	714	180
	12.0	726	713	689	0.56	715	181

The calculated concentration of the uncomplexed (free) Cu^{2+} ions in the solution under investigation diminishes from $10^{-7.6}$ to $10^{-14.6}$ upon increasing the pH from 1.5 to 6.0 (Fig. 1, curve 1) and evidences a rise of the complexing ability of H_2dipic due to its deprotonation (pK_{a1} and pK_{a2} are 2.2 and 4.6, respectively [22]). The further constancy of pCu values at pH over 6.0 is in good agreement with the pK_{a2} value of pyridine-2,6-dicarboxylic acid. No evidence of additional Cu(II) complexation is observed at pH 6.0–12.0, *i. e.* no hydroxy-complexes are formed in the pH region mentioned.

The $E_{1/2}^{r}$ of Cu(II) reduction shifts by –61 mV with a tenfold increase in ligand concentration (*i.e.* from 5 mM to 50 mM) at pH 10.0 suggesting participation of two double-deprotonated $dipic^{2-}$ anions in complex formation. The value of the $Cudipic_2^{2-}$ complex stability constant logarithm calculated from data obtained at pH 6.0–12.0 is equal to 16.1 $\pm$ $\pm$ 0.1, showing Cu(II) complex formation of medium stability. The same mean $log\beta_2$ value ($\pm$ 0.4) was obtained from the data at pH 2.1–5.0, showing the $Cudipic_2^{2-}$ complex predominating in acid solution although protonated H_2dipic and $Hdipic^-$ forms of pyridine-2,6-dicarboxylic acid predominate in the solution bulk. Such phenomenon – predomination of metal ion complex species with a fully deprotonated anion of the ligand under conditions of predominance of the protonated form of the ligand in the solution bulk was obs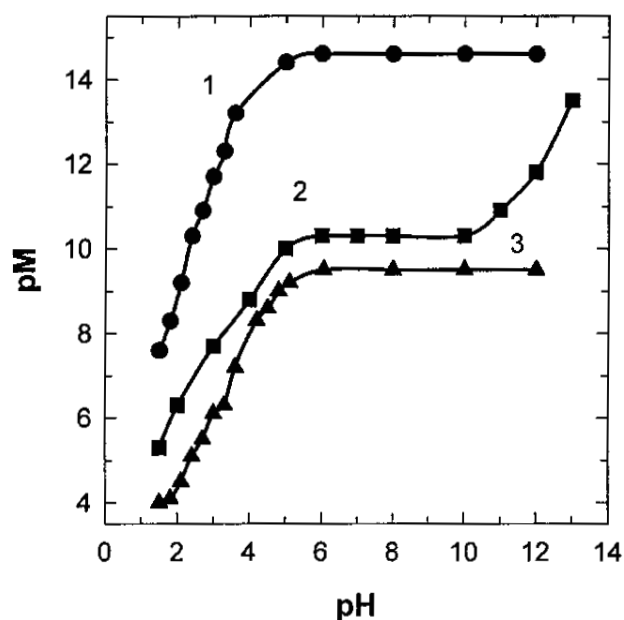erved earlier when investigating Cu(II) complex formation with polyaminopolycarboxylic acids (so-called complexones) [45–47].

The absorption maximum of $Cudipic_2^{2-}$ complex is at λ = 775 nm, the molar extinction coefficient being 60 l mol^{-1} cm^{-1} (Fig. 2, curve 2). A comparison of the spectral characteristics of uncomplexed Cu(II) ions with those of the $Cudipic_2^{2-}$ complex shows a shift of the absorption maximum to shorter wavelengths (from 815 nm to 775 nm) and an increased molar extinction coefficient (from 12 to 60 l mol^{-1} cm^{-1}) (Fig. 2, *cf.* curves 2 and 3).
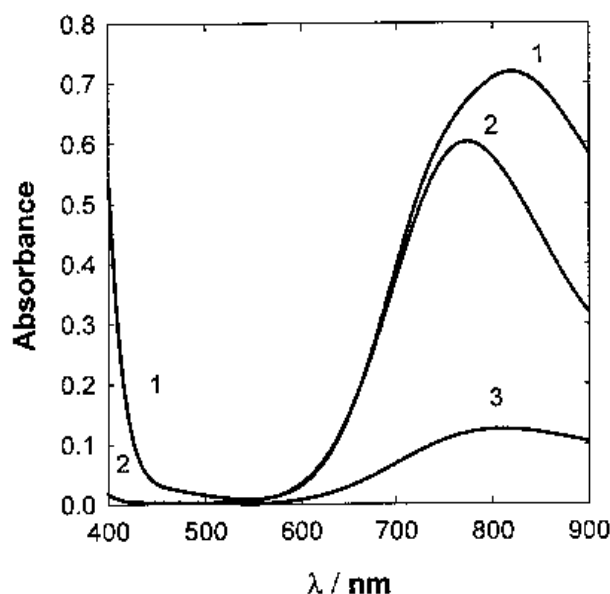

Fig. 2. Light absorption spectra of Cu(II) in presence or absence of pyridinedicarboxylic acids. Solution composition: *1* – 0.01 M $Cu(NO_3)_2$, 0.05 M 4-hydroxypyridine-2,6-dicarboxylic acid, pH 12.0; *2* – 0.01 M $Cu(NO_3)_2$, 0.05 M pyridine-2,6-dicarboxylic acid, pH 10.0; *3* – 0.01 M $Cu(NO_3)_2$, pH 4.0. *I* = 0.4 (KNO_3); 20 °C; 1.0 cm path length quartz cells; pure water used as optical blanc solution

A comparison of the results obtained with Cu(II)–pyridine-2,5-dicarboxylic acid system [48] shows significant differences. The stability of $Cudipic_2^{2-}$ complex is by two orders of magnitude higher than that of Cu(II)–pyridine-2,5-dicarboxylate complex of the same stoichiometry. The higher complexing ability of $dipic^{2-}$ as compared to that of pyridine-2,5-dicarboxylate can be attributed to a different denticity of ligands, *i. e.* pyridine-2,6-dicarboxylate is a tridentate ligand, whereas pyridine-2,5-dicarboxylate is didentate.

The spectral characteristics of the complexes mentioned vary. The molar extinction coefficient value of $Cudipic_2^{2-}$ (ε = 60) is higher than that of Cu(II)–pyridine-2,5-dicarboxylate complex (ε = 47 [48]), the absorption maximum being 775 and 650 nm [48], respectively.

Fig. 1. Dependence of the negative logarithm of free metal ion concentration (pM) on pH in pyridine-2,6-dicarboxylic acid (H_2dipic) containing solutions. Solution composition: $[M(II)]_0$ – 0.5 mM, $[H_2dipic]_0$ – 5 mM. *1* – Cu(II), *2* – Pb(II), *3* – Cd(II). 20 °C; *I* = 0.4 (KNO_3)

Pb(II)–*pyridine-2,6-dicarboxylic acid*

The dependence of $\Delta E_{1/2}^{r}$ of the polarographic waves of Pb(II) reduction in the presence of pyridine-2,6-dicarboxylic acid on pH shows of formation a complex, different from that of Cu(II)–pyridine-2,6-dicarboxylate system (Table 3). The shape of the dependencies is the same up to pH 10.0, $\Delta E_{1/2}^{r}$ values being more positive for Pb(II) (Table 3). Above pH 10 a difference is observed, *i. e.* for Pb(II) a shift of $\Delta E_{1/2}^{r}$ is observed with increasing pH, whereas $\Delta E_{1/2}^{r}$ remains constant in the Cu(II)–pyridine-2,6-dicarboxylate system.

The calculated concentrations of free Pb^{2+} ions reflect changes in $\Delta E_{1/2}^{r}$ depending on solution pH (Fig. 1, curve 2). The pPb decreases from $10^{-7.4}$ to $10^{-10.3}$ upon increasing the pH from 1.5 to 6.0 (Fig. 1, curve 2) and remains constant from pH 6.0 to 10.0. The interpretation of the pPb–pH dependence is the same as for the Cu(II)–pyridine-2,6-dicarboxylate system. The further decrease in pPb at pH over 10.0 shows an additional species form. A comparison of the pPb values at pH 10.0–13.0 with that obtained for $Pb(OH)_3^{-}$ (*i. e.* in the precence of only OH^{-} ions) [49] shows similar pPb levels in the presence and in the absence of pyridine-2,6-dicarboxylate values consistent with the interpretation that Pb(II)–pyridine-2,6-dicarboxylate complex decomposes and converts to trihydroxyplumbate(II).

The $\Delta E_{1/2}^{r}$ of Pb(II) reduction shifts by –60 mV with an increase in ligand concentration from 5 mM to 50 mM at pH 8.0 consistent with the coordination of two double-deprotonated $pdca^{2-}$ anions in complex formation. The $\log\beta_2$ value of the $Pbdipic_2^{2-}$ complex calculated from data obtained at pH 6.0–10.0 is equal to 11.8 ± 0.1 and is in the same range as previously determined [25, 31, 32]. The same mean $\log\beta_2$ value (± 0.2) was obtained from the data at both pH 4.0 and 5.0, showing that the $Pbdipic_2^{2-}$ complex is predominating in weak acid solutions.

Cd(II)–*pyridine-2,6-dicarboxylic acid*

The complexation of Cd(II) ions in pyridine-2,6-dicarboxylate-containing solutions is least efficient from all the metal ions investigated and ranges from $10^{-4.0}$ to $10^{-9.5}$ depending on pH (Fig. 1, curve 3).

The pattern of Cd(II) complex formation with pyridine-2,6-carboxylate is similar to that of Cu(II) complex formation, $E_{1/2}$, $E_{1/2}^{r}$, $\Delta E_{1/2}^{r}$ values being lower (Table 3).

The shift of $\Delta E_{1/2}^{r}$ of Cd(II) reduction from –180 mV to –240 mV as the ligand increases from 5 to 50 mM at pH 10.0 shows that a 1:2 complex $Cddipic_2^{2-}$ forms, and the $\log\beta_2$ value was calculated to 11.0 ± 0.1 (data used from pH 6.0–12).

A similar $\log\beta_2$ value (± 0.3) was calculated from the data obtained at pH 1.8–5.1 and showed the $Cddipic_2^{2-}$ complex to predominate at pH over 1.5.

When comparing the chelating affinities of stereoisomers, *i. e.* pyridine-2,6-dicarboxylate and pyridine-2,5-dicarboxylate, with regard to Cd(II) ions, under the same conditions (initial Cd(II) concentration 0.5 mM and total concentration of ligand 5 mM) at pH 5.0–11 the concentration of free Cd(II) ions is equal to $10^{-9.5}$ and $10^{-5.4}$, respectively (*cf.* this work and [48]). The higher chelating affinity of pyridine-2,6-dicarboxylate ions can be explained by the above-mentioned differences in the denticity of ligands as well as by a different stoichiometry of the complexes formed, *i. e.* Cd(II) forms a diligand complex with pyridine-2,6-dicarboxylate, whereas in the case of pyridine-2,5-dicarboxylate the monodentate complex with $\log\beta_1 = 4.5$ is formed.

Diffusion coefficients of Cu(II), Pb(II) *and* Cd(II) *complexes with pyridine-2,6-dicarboxylate*

The diffusion coefficients of 1:2 complexes of Cu(II), Pb(II) and Cd(II) with $dipic^{2-}$ in 0.4 M KNO_3 solution were calculated from polarographic data as described in equation 3. The diffusion coefficient values are listed in Table 4. The highest diffusion coefficient was obtained for $Cddipic_2^{2-}$, followed by $Pbdipic_2^{2-}$ and $Cudipic_2^{2-}$ species.

The diffusion coefficient of Cd(II) ions in pyridine-2,6-dicarboxylate solutions (7.1×10^{-6} cm^2 s^{-1}, Table 4) is lower than in pyridine-2,5-dicarboxylate solutions in the same conditions (7.8×10^{-6} cm^2 s^{-1} [48]) and is in agreement with the complex stoichiometry.

Table 4. **Diffusion coefficient values of metal ion species with pyridine-2,6-dicarboxylate (dipic^{2-}) calculated from polarographic data ($I = 1.0$; 20 °C)**

Solution composition, mM	Predominating complex compound	$D \times 10^6$, cm^2 s^{-1}
$[Cu(II)]_0 = 0.5$, $[H_2dipic]_0 = 5$; pH 6.0–12.0	$Cudipic_2^{2-}$	5.2
$[Pb(II)]_0 = 0.5$, $[H_2dipic]_0 = 5$; pH 6.0–10.0	$Pbdipic_2^{2-}$	5.4
$[Cd(II)]_0 = 0.5$, $[H_2dipic]_0 = 5$; pH 6.0–12.0	$Cddipic_2^{2-}$	7.1

Metal ion complexes with 4-hydroxypyridine-2,6-dicarboxylic acid

The diffusion-controlled, quasi-reversible polarographic waves of Pb(II) and Cd(II) reduction in the presence of 4-hydroxypyridine-2,6-dicarboxylic acid are observed only in acid solutions at pH 1.5–5.0 (Table 5). In the case of Cu(II) such waves are observed both at pH 1.5–5.0 and 12.0–13.0 (Table 5).

The $E_{1/2}$, $E_{1/2}^r$, $\Delta E_{1/2}^r$ as well as free metal ion concentration values are more positive in acidic 4-hydroxypyridine-2,6-dicarboxylate solutions than those obtained in pyridine-2,6-dicarboxylate solutions in the same conditions (*cf.* Figs. 1 and 3, and Tables 3 and 5), suggesting that the coordination ability of pyridine-2,6-dicarboxylic acid with OH-group is lower. Since both ligands are tridentate and the coordination of metal ions occurs in the same way through one nitrogen and two oxygen atoms, the lower complexing ability of 4-hydroxypyridine-2,6-dicarboxylic acid compared with that of pyridine-2,6-dicarboxylic acid can be atributed to the influence of the substituent – OH-group. The OH-group in 4-hydroxypyridine-2,6-dicarboxylic acid pulls electrons from the

Table 5. **Characteristics of the process of metal ion reduction on a DME in solutions of 4-hydroxypyridine-2,6-dicarboxylic acid ($[M(II)]_0$ = 5 mM; $[H_3chel]_0$ = 50 mM; 20 °C; I = 0.4)**

| Metal ion	pH	$-E_{1/2}$, mV	$E_{1/2}^{'}$–, mV	$-E_{1/2}$, mV	α	$-E_{1/2}^r$, mV	$-\Delta E_{1/2}^r$, mV
Cu(II)	1.5	11	4	–30	0.55	–8	56
	2.0	49	41	8	0.56	30	94
	5.0	115	110	73	0.64	89	156
	12.0	428	417	393	0.63	418	481
	13.0	425	414	389	0.73	415	480
Pb(II)	1.5	382	378	347	0.74	364	22
	2.0	403	401	369	0.83	376	35
	3.0	416	414	378	0.74	385	43
	5.0	454	448	419	0.67	440	101
Cd(II)	1.5	551	539	516	0.48	542	8
	2.0	552	545	518	0.58	543	9
	3.0	571	565	534	0.49	558	25
	4.0	590	580	548	0.31	574	40
	5.0	593	588	554	0.25	580	48
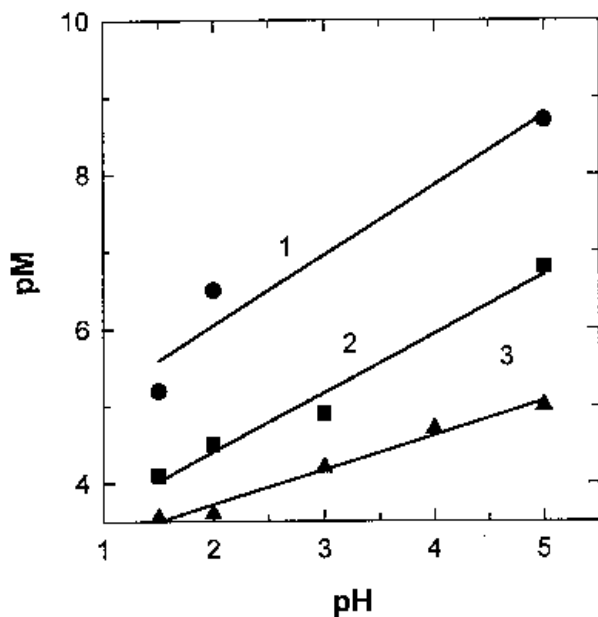
Fig. 3. Dependence of the negative logarithm of free metal ion concentration (pM) on pH in 4-hydroxypyridine-2,6-dicarboxylic acid (H$_3$chel) containing solutions. Solution composition: $[M(II)]_0$ – 0.5 mM, $[H_3chel]_0$ – 5 mM. *1* – Cu(II), *2* – Pb(II), *3* – Cd(II). 20 °C; I = 0.4 (KNO$_3$).

pyridine ring and reduces the coordination ability of this ligand.

In alkaline solutions the complexing ability of 4-hydroxypyridine-2,6-dicarboxylate is higher than that of pyridine-2,6-dicarboxylate. The $\Delta E_{1/2}^r$ value of Cu(II) reduction is by *ca.* 150 mV more negative in the case of 4-hydroxypyridine-2,6-dicarboxylic acid at pH 12 (Tables 3 and 5). 4-hydroxypyridine-2,6-dicarboxylic acid (H$_3$chel) exists in the solution as a triple-deprotonated anion due to the deprotonation of OH-group in alkaline solutions (pK_{a3} = 10.9 [22]) and forms a 1:2 complex with Cu(II), *i. e.* CuChel$_2^{4-}$. The calculated stability constant (logβ_2 = 21.5 ± 0.2) is high, and 4-hydroxypyridine-2,6-dicarboxylic acid can be attributed to the group of ligands forming stable complexes with Cu(II) ions, *e. g.,* polyaminopolycarboxylic acids [45–47]. The diffusion coefficient calculated from the polarographic data for the complex equals 3.9 × 10^{-6} cm^2 s^{-1}.

The absorption maximum of Cuchel$_2^{4-}$ complex is at λ = 820 nm, the molar extinction coefficient being 72 l mol^{-1} cm^{-1} (Fig. 2, curve 1). The λ_{max} is shifted to longer wavelengths with an increase in the molar

extinction coefficient compared to Cudipic$_2^{2-}$ (*cf.* curves 1 and 2 in Fig. 2).

The stability of Cuchel$_2^{4-}$ and Cudipic$_2^{2-}$ varies more than by four orders of magnitude with the logβ_2 ranging from 21.5 to 16.1, respectively. The enhanced complexing ability of 4-hydroxypyridine-2,6-dicarboxylic acid in alkaline solutions compared with that of pyridine-2,6-dicarboxylic acid can be explained by the influence of the OH-group substitute. The deprotonated OH-group in 4-hydroxypyridine-2,6-dicarboxylic acid acts as a donor of electrons to the pyridine ring and increases the coordination ability of the ligand.

CONCLUSIONS

1. In solutions with excess of ligand Cu(II), Pb(II) and Cd(II) form 1:2 complexes with the tridentate dianion of pyridine-2,6-dicarboxylic acid (dipic^{2-}) from weak acid to alkaline solutions. The values of logβ_2 for Cu(II), Pb(II) and Cd(II) are 16.1, 11.8 and 11.0, respectively. Tenfold excess of pyridine-2,6-dicarboxylic acid reduces the concentration of free Cu(II), Pb(II) and Cd(II) ions from 1 to 11 orders of magnitude, depending on the pH and stability constant of the complex formed. The values of the diffusion coefficients for Cu(dipic)$_2^{2-}$, Pb(dipic)$_2^{2-}$ and Cd(dipic)$_2^{2-}$ are equal to 5.4×10^{-6}, 5.2×10^{-6} and 7.1×10^{-6} cm^2 s^{-1} , respectively.

2. Pyridine-2,6-dicarboxylic acid forms more stable complexes with metal ions than does pyridine-2,5-dicarboxylic acid. The higher complexing ability of pyridine-2,6-dicarboxylate compared to that of pyridine-2,5-dicarboxylate can be attributed to a different denticity of ligands; *i. e.* pyridine-2,6-dicarboxylate acts as a tridentate ligand, whereas pyridine-2,5-dicarboxylate is didentate.

3. The complexing ability of 4-hydroxypyridine-2,6-dicarboxylic acid is lower in acid solutions and higher in alkaline solutions than that of pyridine-2,6-dicarboxylic acid. This difference is attributed to the different action of the substituent, *i. e.* OH-group, depending on solution pH. In acid solutions OH-group acts as an electron acceptor and decreases the electron donation available to the nitrogen atom in 4-hydroxypyridine-2,6-dicarboxylic acid, whereas in alkaline solution OH-group is deprotonated, and the deprotonated O$^-$ group acts as an electron donor and increases the coordination ability of the ligand.

4. The triple-deprotonated anion of 4-hydroxypyridine-2,6-dicarboxylic acid (chel^{3-}) forms a stable di-ligand complex with Cu(II), the stability constant logarithm being 21.5 ± 0.2. The diffusion coefficient for Cuchel$_2^{4-}$ complex is 3.9×10^{-6} cm^2 s^{-1}.

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CU(II), PB(II) IR CD(II) KOMPLEKSŲ SU PIRIDIN-2,6-DIKARBOKSILATU IR 4-HIDROKSIPIRIDIN-2,6-DIKARBOKSILATU SUSIDARYMAS VANDENINIUOSE TIRPALUOSE

S a n t r a u k a

Nuolatinės srovės poliarografijos metodu (20°C; $I = 0,4$ (KNO_3)) tiriant sunkiųjų metalų jonų sąveiką su piridin-2,6-dikarboksirūgštimi ir 4-hidroksipiridin-2,6-dikarboksirūgštimi nustatyta, kad Cu(II), Pb(II) ir Cd(II) su visiškai deprotonizuotu piridin-2,6-dikarboksirūgšties anijonu sudaro 1:2 kompleksus. Apskaičiuotosios kompleksų patvarumo konstantos logaritmų (logβ_2) vertės atitinkamai lygios 16,1, 11,8 ir 11,0. Cu(II) su visiškai deprotonizuotu 4-hidroksipiridin-2,6-dikarboksirūgšties anijonu sudaro patvarų 1:2 kompleksą, kurio logβ_2 = 21,5. Pagal poliarografinius duomenis apskaičiuotos identifikuotų kompleksų difuzijos koeficientų vertės. Nustatyta, kad rūgštinėje terpėje piridin-2,6-dikarboksirūgštis stipriau kompleksina minėtus katijonus, tuo tarpu šarminėje terpėje 4-hidroksipiridin-2,6-dikarboksilato anijono kompleksinanti geba yra didesnė.