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Original Scientific Paper

## Potentiometric Determination of Stability Constants of 2,3-Dihydroxypropanoate Complexes of Zinc(II), Cadmium(II), and Lead(II)

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Stability constants of 2,3-dihydroxypropanoate complexes of zinc(II), cadmium(II) and lead(II) were determined by potentiometric titration in buffer solution using glass and quinhydrone electrodes. All measurements were carried out at  $(298.2 \pm 0.1)$  K in buffer solutions of constant ionic strength of  $2 \text{ mol dm}^{-3}$ . Stability constants and their 95 per cent confidence intervals were calculated on a digital computer using an algorithm described elsewhere<sup>11</sup>. On the basis of the obtained stability constants, different factors governing the stability of the investigated complexes were discussed.

Only a few papers have so far dealt with the stability of 2,3-dihydroxypropanoate complexes<sup>1,2,3</sup>. In the present paper the stability of 2,3-dihydroxypropanoate complexes of zinc(II), cadmium(II) and lead(II) are given. This study was performed as a continuation of a systematic investigation of metal complexes with hydroxy substituted and unsubstituted monocarboxylate ion<sup>2-12</sup>, in order to give some insight into the correlation between the stability of the complexes and the nature of the central metal ion, the basicity of the ligand and the position of the hydroxy group substitution.

### EXPERIMENTAL

Sodium 2,3-dihydroxypropanoate was prepared from the corresponding acid by neutralization with sodium hydroxide (10 per cent solution in methanol). A large amount of solid impurities were removed from the methanol solution by filtration. Methanol was then removed by vacuum distillation. Sodium 2,3-dihydroxypropanoate was dissolved in water, and the aqueous solution was purified with activated charcoal.

Preparation of metal perchlorates and buffer solutions was the same as previously described<sup>3</sup>.

Potentiometric measurement was carried out continuously as described elsewhere.<sup>11</sup>

All measurements were performed at  $(298.2 \pm 0.1)$  K in buffer solution of a constant ionic strength of  $2 \text{ mol dm}^{-3}$  obtained by the addition of sodium perchlorate.

Each complex system was measured both with a combined glass electrode (Metrohm EA 153 with reference electrode Ag/AgCl in  $2 \text{ mol dm}^{-3}$  NaCl) and with a quinhydrone electrode (vs. reference solution containing  $20 \text{ mmol dm}^{-3}$  HClO<sub>4</sub> and  $1980 \text{ mmol dm}^{-3}$  NaClO<sub>4</sub>).

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The concentration of zinc(II) and cadmium(II) was 50 and 100 mmol dm<sup>-3</sup>, while that of lead(II) was 20 and 40 mmol dm<sup>-3</sup>. Buffer solutions with two acid-to-salt ratios 1:1 and 0.3:1 were prepared for each metal ion concentration.

### RESULTS AND DISCUSSION

The behaviour of both electrodes was tested prior to potentiometric complex formation measurements. By adding metal perchlorates to the reference solution (i. e. by diluting HClO<sub>4</sub> in the reference solution) some deviations,  $\delta$  from the Nernst equation were observed (Table I). In Table I the minus sign means

TABLE I  
*Potential Deviations from the Nernst Equation*

Metal ion	$\delta/\text{mV mol}^{-1}$	
	Quinhydrone electrode <sup>a</sup>	Glass electrode <sup>b</sup>
Na <sup>+</sup>	0	0
Zn <sup>2+</sup>	-6	+8
Cd <sup>2+</sup>	-10	+2
Pb <sup>2+</sup>	-10	+2

<sup>a</sup> 2 mol dm<sup>3</sup> NaClO<sub>4</sub> in salt bridge

<sup>b</sup> 2 mol dm<sup>3</sup> NaCl in salt bridge

that the observed value was smaller and the plus sign means that this value was greater than the value calculated from the Nernst equation. Different deviations were obtained by using two different electrolyte solutions in the salt bridge suggesting that these deviations can partially be attributed to liquid junction potentials, complex formation with quinhydrone, metal error of glass electrode etc. Therefore, potential functions measured with glass and quinhydrone electrodes were different as a result of complex formation (i. e. the difference in potential measured in presence and absence of metal ion for different ligand concentration): 14 mV mol<sup>-1</sup> for zinc(II) and 12 mV mol<sup>-1</sup> for cadmium(II) and lead(II), by using a quinhydrone and a glass electrode, respectively. However, by using a lower metal ion concentration the difference in potential measured with the glass and with the quinhydrone electrode is proportionally smaller and is reflected in the values of the stability constants, obtained from separate measurements using each of the two electrodes. Good agreement of these values (Table II) indicates that the potential deviations have a negligible effect upon stability constants determination.

Transformed formation functions (Figure 1) for both metal ion concentrations and both acid-to-salt ratios clearly demonstrate the absence of polynuclear and/or mixed hydroxy complexes.

Stability constants and their 95 per cent confidence intervals measured with each electrode calculated with a digital computer by means of the algorithm described elsewhere<sup>11</sup> are given in Table II together with corresponding mean values of stability constants.

TABLE II  
Stability Constants of 2,3-Dihydroxypropanoate Complexes

Metal ion	Electrode	$\lg \frac{K_1}{\text{dm}^3 \text{mol}^{-1}}$	$\lg \frac{\beta_2}{\text{dm}^6 \text{mol}^{-2}}$	$\lg \frac{\beta_3}{\text{dm}^9 \text{mol}^{-3}}$
Zn <sup>2+</sup>	qh	1.47 ± 0.02	2.35 ± 0.02	2.82 ± 0.02
	gl	1.44 ± 0.02	2.36 ± 0.02	2.55 ± 0.02
	mean value	1.46 ± 0.02	2.36 ± 0.01	2.69 ± 0.14
Cd <sup>2+</sup>	qh	1.27 ± 0.04	2.20 ± 0.04	2.66 ± 0.04
	gl	1.23 ± 0.02	2.13 ± 0.02	2.75 ± 0.02
	mean value	1.25 ± 0.01	2.17 ± 0.04	2.71 ± 0.05
Pb <sup>2+</sup>	qh	2.10 ± 0.03	3.23 ± 0.03	3.39 ± 0.03
	gl	2.09 ± 0.02	3.29 ± 0.02	3.56 ± 0.02
	mean value	2.10 ± 0.01	3.26 ± 0.03	3.48 ± 0.09

In Table III stability constants of monoligand complexes are compared with monohydroxy substituted and unsubstituted propanoate complexes with the same metal ions all obtained by means of the quinhydrone electrode.  $\text{p}K_A$  values are listed in the same Table for corresponding carboxylic acids as a measure of the basicity of ligands.

All 2-hydroxypropanoate complexes have greater stability than unsubstituted propanoate complexes despite lower basicity of the former, which can be explained by bidentate coordination of 2-hydroxypropanoate complexes (i. e. additional chelate stabilization). The contribution of the OH group in position 3 to the additional chelate stabilization is negligible, as expected. The basicity of 2,3-dihydroxypropanoate ligand is lower due to the induction effect of the OH group in position 3. Therefore, the stability of zinc(II) 2,3-dihydroxypropanoate complexes is expected to be lower than the stability of zinc(II) 2-hydroxypropanoate complexes. However, it was found that the stability of zinc(II) 2,3-dihydroxypropanoate complexes is even lower than expected, which can

TABLE III  
Stability Constants of Monoligand Complexes

Ligand	$\text{p}K_A^*$	$\lg \frac{K_1}{\text{dm}^3 \text{mol}^{-1}}$		
		Zn(II)	Cd(II)	Pb(II)
2,3-Dihydroxypropanoate	3.54	1.47 ± 0.02	1.27 ± 0.04	2.10 ± 0.03
2-Hydroxypropanoate <sup>12</sup>	3.86	1.67 ± 0.01	1.29 ± 0.02	2.16 ± 0.02
3-Hydroxypropanoate <sup>12</sup>	4.57	0.86 ± 0.02	1.28 ± 0.04	2.10 ± 0.02
Propanoate <sup>4</sup>	4.89	1.00 ± 0.02	1.23 ± 0.03	2.07 ± 0.06

\* Our measurement results.

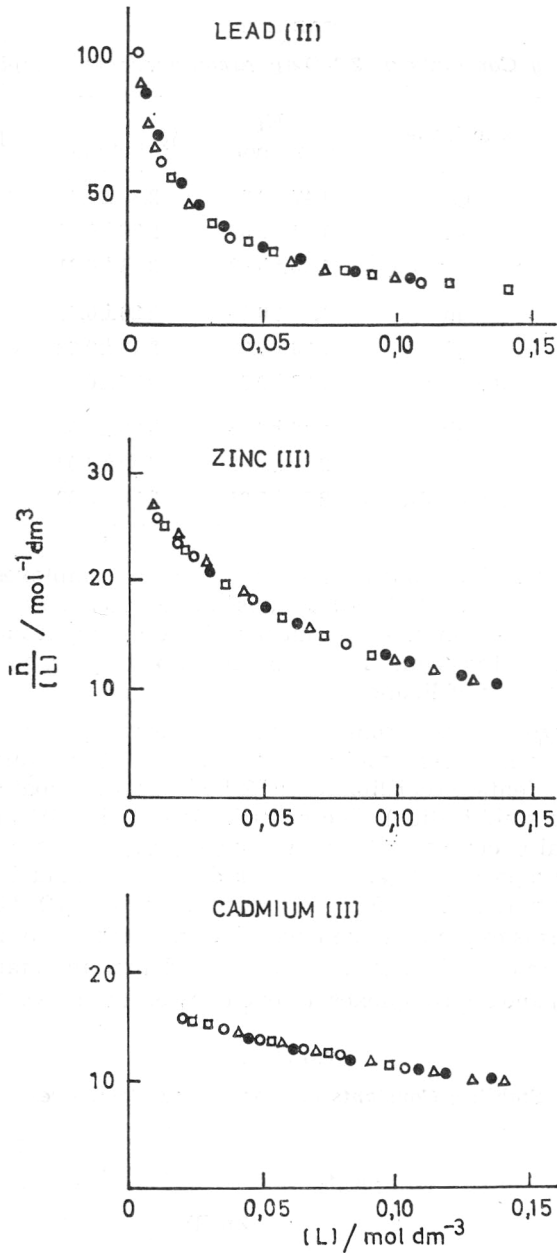


Figure 1.  $n/[L]$  vs.  $[L]$  curves for different metal ion concentration and different acid-to-salt ratio in buffer solutions

	Acid-to-salt ratio	$c_{M^{2+}}$ mol $\text{dm}^{-3}$
□	0.3 : 1	100 <sup>a</sup>
●	0.3 : 1	50 <sup>b</sup>
○	1 : 1	100 <sup>a</sup>
△	1 : 1	50 <sup>b</sup>

<sup>a</sup> 40 mmol  $\text{dm}^{-3}$  for  $\text{Pb}^{2+}$

<sup>b</sup> 20 mmol  $\text{dm}^{-3}$  for  $\text{Pb}^{2+}$

be explained by additional inductive weakening of chelate coordination of the OH group in position 2 by the OH group in position 3.

The latter effect is negligible in cadmium(II) and lead(II) 2,3-dihydroxypropanoate complexes.

The quantitative analysis of different effects governing the stability of metal ion monocarboxylato complexes will be published elsewhere.

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## SAŽETAK

**Potencimetrijsko određivanje konstanti stabilnosti  
2,3-dihidroksipropanoato-kompleksa cinka(II), kadmija(II) i olova(II)**

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Konstante stabilnosti 2,3-dihidroksipropanoato-kompleksa cinka(II), kadmija(II) i olova(II) određene su potencimetrijskom titracijom u puferkim otopinama konstantne ionske jakosti  $2 \text{ mol dm}^{-3}$  uz primjenu staklene i kinhidronske elektrode. Konstante stabilnosti i njihovi intervali 95% -tne vjerojatnosti izračunane su s pomoću digitalnog računala. Na temelju dobivenih rezultata prodiskutirana je stabilnost istraživanih kompleksa s obzirom na bazičnost liganda.

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