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The Investigation of the Stability of 2-Oxopropanoate Complexes of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II), and Lead(II) in Aqueous Solutions

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Stability constants of 2-oxopropanoate complexes of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), and lead(II) were determined using potentiometric and spectrophotometric methods at a constant ionic strength of 2 mol dm^{-3} ($NaClO_4$). Experimental data were evaluated on a digital computer using a weighted least squares algorithm.

Continuing the systematic investigation of the influence of different monocarboxylate ion substituents on its donor properties[1-9], the stabilities of some bivalent metal ion complexes with 2-oxopropanoate ion (pyruvate ion) were investigated. In the present as in all previous investigations the ionic strength was kept constant in order to compare the stability of complexes on the basis of concentration stability constants.

The instability of buffer solutions of 2-oxopropanoic acid (pyruvic acid) due to catalyzed dimerization of both acid and its anion in the presence of metal ions is well known[10,11]. Therefore it was necessary to find out experimental conditions suitable for stability constant measurements of the monomer 2-oxopropanoate ion. The NMR investigations[10] of the pyruvate complex of zinc(II) have demonstrated that in the solution both tautomeric forms (keto and enolic) of the ligand were present. Both tautomeric forms, however, showed very weak chelate effect[11] and it was found that at low pH values in fresh solution only the keto form of 2-oxopropanoate ion exsists[12].

EXPERIMENTAL

The buffer solutions were prepared from sodium 2-oxopropanoate of known concentration determined by potentiometric titration with perchloric acid in glacial acetic medium. 2-Oxopropanoic acid was prepared immediately prior to measurements by adding a known amount of perchloric acid to the sodium salt solution. Metal ion solutions were prepared from corresponding perchlorates.

All measurements were performed at (298.2 ± 0.1) K in solutions with a constant ionic strength of 2 mol dm^{-3} obtained by the addition of $NaClO_4$.

Potentiometric measurements were performed with buffer solutions with 1 : 10 and 3 : 10 acid-to-salt ratios. A relatively low acid concentration in the buffer solution was necesary due to the relatively low pK_A value of the 2-oxopropanoic acid. Our

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measurements result performed in the present investigation resulted a pK_A value of 2.27. The pH of the all investigated systems was between 2.6 and 3.5. Spectrophotometric measurements were performed using only a 1 : 10 acid-to-salt ratio in buffer solutions.

Metal ion concentrations in buffer solutions were: 20 and 40 mmol dm^{-3} for copper(II) and lead(II) complexes, respectively 50 and 100 mmol dm^{-3} for cobalt(II), nickel(II), zinc(II) and cadmium(II) complexes for potentiometric measurements, while concentrations of 20 and 120 mmol dm^{-3} for cobalt(II) and nickel(II) complexes and 5 and 30 mmol dm^{-3} for copper(II) complexes were applied for spectrophotometric measurements.

The dimerization catalyzed by metal ion present in the solution is relatively slow and it is manifested by a slow increase of the pH of the solution during potentiometric measurements or by a slow change of the absorbance during spectrophotometric measurements. These changes were observed with copper(II) and lead(II) ion after 1 minute and with all other metal ions used after 10 minutes, suggesting that copper(II) and lead(II) catalyze the dimerization in the greatest extent. Within these intervals the pH and the absorbance of the investigated complex solutions remained constant within the error of measurement. All systems except that of copper(II) 2-oxopropanoate complexes were measured by continuous potentiometric titrations[7] while copper(II) and lead(II) complexes due to their instability were measured by discontinuous potentiometric measurements. The solution containing copper(II) ion was added to the buffer solution immediately before measurements. The reproducibility of the measured potential was within 0.2 mV with both continuous and discontinuous potentiometric measurements; it was only necessary to prepare fresh solutions with low pH and to measure the potential (absorbance) within the mentioned intervals.

Spectrophotometric measurements of buffer solutions of cobalt(II), nickel(II) and copper(II) were done discontinuously[12] due to the above mentioned reasons. Figure 1. shows the absorbtion spectra of Co(II), Ni(II) and Cu(II) solutions. The folowing wavelength were selected for spectrophotometric stability constant measurements: 520 nm, 670 nm and 760 nm for Co(II), Ni(II) and Cu(II) complexes, respectively. The buffer solutions and the solution of the metal ion were thermostated, thus absorbance measurements could be performed within few minutes after the preparation of the fresh solution.

Apparatus. — Potentiometric measurements were carried out with glass and quinhydrone electrodes using potentiograph E436 (Metrohm) as described elsewhere[9].

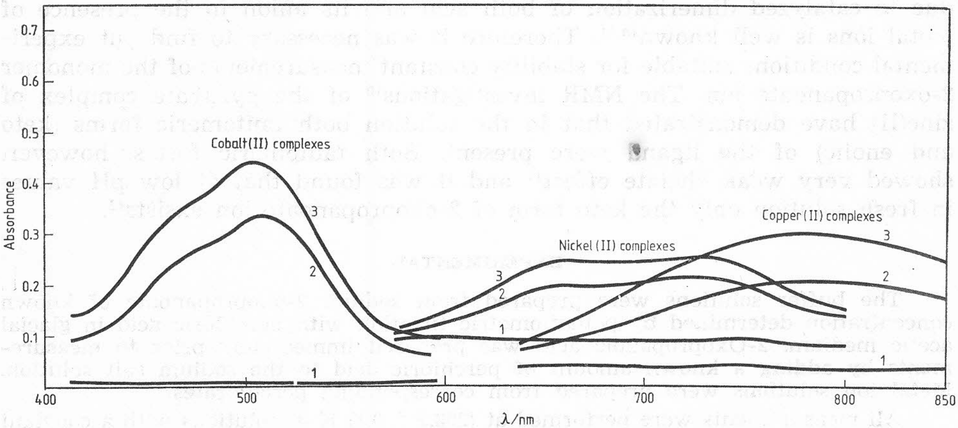

Figure 1. Absorption spectra of investigated solutions.

(1) Buffer solutions without metal ion
(2) Solutions of metal ion without ligand
(3) Buffer solutions with metal ion
C_M = 20 mmol dm^{-3} for Co(II) and Ni(II) solutions and 5 mmol dm^{-3} for Cu(II) solutions
C_L = 100 mmol dm^{-3} for Co(II) and Ni(II) complexes and 50 mmol dm^{-3} for Cu(II) complexes
$C_{HL} : C_L = 1 : 10$; $I = 2$ mol dm^{-3} (NaClO$_4$); $d = 3$ cm

Spectrophotometric measurements were carried out on either Acta III (Beckman) spectrophotometer or VSU-1 (Carl Zeiss) spectrophotometer, both having thermostated cells.

RESULTS AND DISCUSSION

Using glass and quinhydrone electrodes as indicator electrodes for potentiometric complex formation measurements, deviations from Nernst equation were reported for zinc(II), cadmium(II) and lead(II) ions[18]. These deviations are found when the Na(I) ion in the supporting electrolyte ($NaClO_4$) was substituted with increased metal ion concentration. The same was found in this work for cobalt(II), nickel(II) and copper(II) ions (Table I). These deviations have been taken into account when calculating stability constants.

TABLE I

Potential Deviations from the Nernst Equation

Metal ion	δ/mV mol^{-1}	
	Quinhydrone electrode[a]	Glass electrode[b]
Co^{2+}	9	3
Ni^{2+}	8	4
Cu^{2+}	7	5

[a] 2 mol dm^{-3} $NaClO_4$ in salt bridge

[b] 2 mol dm^{-3} NaCl in salt bridge

All experimental data were evaluated on a PDP-8 minicomputer in extended precision (10.5 significant digits) using the weighted least squares method[5,7]. For both the potentiometric method and Bjurrum's spectrophotometric method of corresponding solutions[5], the average number of ligands, $\bar{n}$, bound per one metal ion were calculated together with the free ligand concentration, [L]. From these data a polynomial $F_o([L]) = 1 + \sum_{i=1}^{N} \beta_i [L]^i$, determining the unknown cumulative stability constants, can be easily calculated[5]. By weighted least squares polynomial fitting cumulative stability constants, β_i, and their 95 per cent confidence intervals were obtained.

From transformed formation functions obtained by potentiometric measurements using glass electrode (Figure 2), it can be seen that quite a good agreement was achieved for different metal ion concentrations and different acid-to-salt ratios (experimental points that coincide have been represented by only one symbol). In the same time these results prove the absence of polynuclear and/or mixed hydroxy complexes.

Logarithmic values of stability constants with their 95 per cent confidence intervals are listed ni Table II. Values obtained by different methods are in a very good agreement with those found by others[11].

On the basis of the stability constants of monoligand complexes, the stability of the investigated systems was found to follow the same order as stated in this laboratory for all other unsubstituted and substituted monocarboxylate complexes.

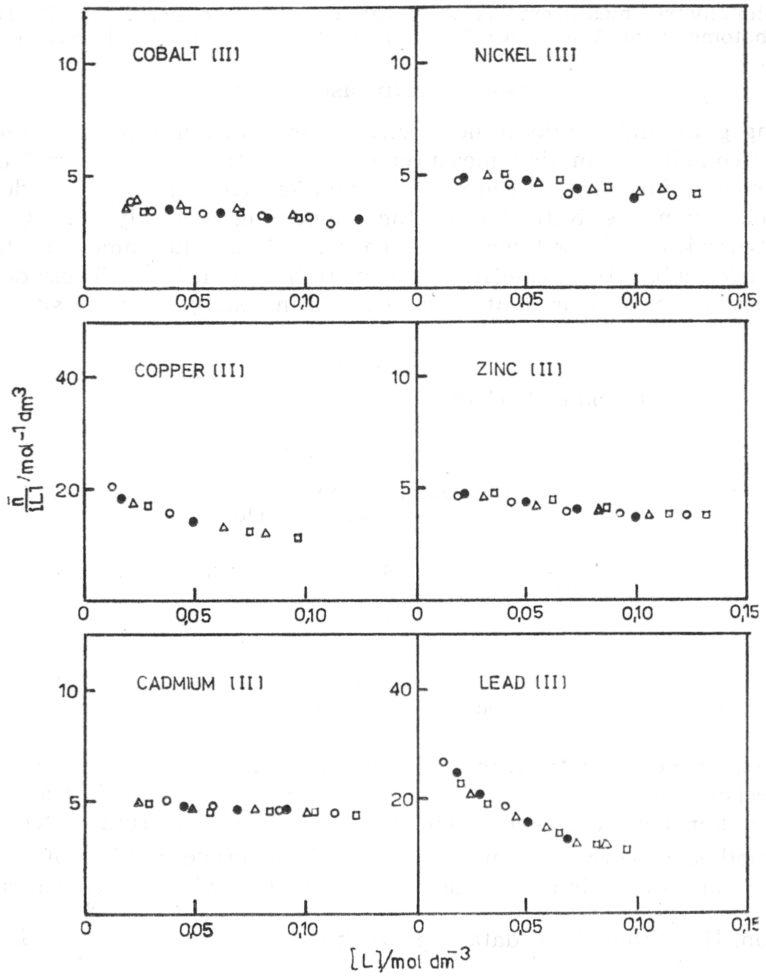

Figure 2. $\bar{n}/[L]$ vs. [L] curves for two metal ion concentrations and two acid-to-salt ratios obtained with glass indicator electrode.

C_M/mol dm^{-3}	C_M/mol dm^{-3}	Acid-to-salt ratio
● 0.05	○ 0.10	1 : 10
□ 0.05	△ 0.10	3 : 10

2-Oxopropanoate complexes of the investigated bivalent metal ions are very weak which is in accordance with the low basicity of the ligand involved ($pK_A = 2.27$). Therefore the stability of these complexes is governed mainly by the ligand basicity. By comparing the monoligand stability constants of cobalt(II) and nickel(II) unsubstituted propanoate complexes[15], 2-hydroxypropanoates[9] and 2-oxopropanoates obtained in this work (Table III) it can be seen that despite the lower basicity 2-oxopropanoate complexes of cobalt (II) and nickel(II) have almost identical stability as unsubstituted propanoate complexes suggesting that there is a very small additional contribution to the stability[11].

TABLE II

Stability Constants of 2-Oxopropanoate Complexes
$I = 2$ mol dm^{-3} ($NaClO_4$)

Metal ion	Methods	log K_1	log β_2
Co^{2+}	Pot. (GE)*	0.60 ± 0.02	0.44 ± 0.03
	Pot. (QE)**	0.61 ± 0.02	0.59 ± 0.03
	Spe.	0.71 ± 0.04	1.31 ± 0.04
	Mean value	0.64	0.77
Ni^{2+}	Pot. (GE)	0.73 ± 0.02	0.81 ± 0.03
	Pot. (QE)	0.72 ± 0.02	0.83 ± 0.03
	Spe.	0.82 ± 0.02	
	Mean value	0.76	0.83
Cu^{2+}	Pot. (GE)	1.35 ± 0.01	2.05 ± 0.02
	Pot. (QE)	1.41 ± 0.01	2.03 ± 0.02
	Spe.	1.39 ± 0.03	
	Mean value	1.38	2.04
Zn^{2+}	Pot. (GE)	0.72 ± 0.02	0.54 ± 0.03
	Pot. (QE)	0.76 ± 0.02	0.80 ± 0.03
	Mean value	0.74	0.67
Cd^{2+}	Pot. (GE)	0.69 ± 0.01	1.07 ± 0.02
	Pot. (QE)	0.71 ± 0.02	1.19 ± 0.02
	Mean value	0.70	1.13
Pb^{2+}	Pot. (GE)	1.50 ± 0.02	2.25 ± 0.02
	Pot. (QE)	1.51 ± 0.02	2.30 ± 0.02
	Mean value	1.51	2.28

* GE = Glass electrode

** QE = Quinhydrone electrode

TABLE III

Stability Constants log K_1 *of Monoligand Complexes*

Ligand / Metal ion	Propanoate[15]	2-Oxopropanoate	2-Hydroxopropanoate[9]
Co^{2+}	0.78	0.64	1.28
Ni^{2+}	0.86	0.76	1.57
pK_A	4.87	2.27	3.79

It is necessary to point out that our values of stability constants determined for 2-oxopropanoate complexes of bivalent metal ions are lower than some of the values reported in the literature[12,17]. Leussing and Stanfield[10] have found from NMR studies of zinc(II) 2-oxopropanoate complex that the stability of this monoligand complex with the keto form of the ligand (log $K_1 = 1.0$) is much lower than the stability of the complex with the enolic form of the ligand (log $K_1 = 2.5$). Our measurements were all taken immediately after preparing the fresh solutions ensuring to have mainly keto form of the ligand[12]. Comparing our value of stability constants of zinc(II) 2-oxopropanoate complex ($\log K_1 = 0.80$) with that of Leussing and Stanfield[10] obtained for keto form of the ligand, it can be seen that a good agreement is obtained. The same is true for pK_A values (our value $pK_A = 2.27$ and those found by Leussing et al. for the keto form $pK_A = 2.02$[10] and $pK_A = 2.39$[11]). The presence of enolic form of ligand ($pK_A = 3.60$ for the enolic form of pyruvic acid[10]) in buffer solutions of 2-oxopropanoic acid can account for higher stability constant values reported in the literature[12,17]. Different ionic strength supporting electrolyte, pH, method etc. can also contribute to these discrepancies in stability constants.

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SAŽETAK

Istraživanje stabilnosti 2-oksopropanoato-kompleksa kobalta(II), nikla(II), bakra(II), cinka(II), kadmija(II) i olova(II) u vodenim otopinama

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Potenciometrijskom i spektrofotometrijskom metodom određene su konstante stabilnosti 2-oksopropanoatokompleksa divalentnih metalnih iona navedenih u naslovu. Ionska jakost istraživanih sistema bila je 2 mol dm^{-3} ($NaClO_4$). Eksperimentalni rezultati obrađeni su metodom najmanjih kvadrata s pomoću digitalnog računala.

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