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Spectrophotometric Determination of Stability Constants of Lactato and β -Hydroxypropionato Complexes of Cobalt(II), Nickel(II), and Copper(II)*

J. Savić, M. Savić, and I. Filipović

*Institute of Chemistry, University of Sarajevo, 71000 Sarajevo,
Bosnia and Hercegovina,*

and

*Institute of Inorganic and Analytical Chemistry, University of Zagreb,
41000 Zagreb, Croatia, Yugoslavia*

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Stability constants for lactato and β -hydroxypropionato complexes of Co(II), Ni(II), and Cu(II) were obtained from spectrophotometric data, using Bjerrum's method of corresponding solutions. Measurements were made in the visible range and the results plotted for graphical evaluation by Fronaeus' method. Graphically determined values for each stability constant were utilized for averaging and least-squares calculations with a digital computer programmed according to R. S. Tobias («Gauss Z» program).

So far only a few papers have dealt with stabilities of complexes formed by cobalt, nickel, and copper with ions derived from hydroxycarboxylic acids¹⁻⁸. Lactato complexes of these metals have been examined by conductometric¹, potentiometric²⁻⁴, polarographic⁵, ion-exchange³, and spectrophotometric methods^{6,7}; less work has been devoted to β -hydroxypropionato complexes, which have only been studied by solubility⁸, and spectrophotometric methods⁷.

The present work is concerned with an attempt to obtain comparable values for the stability constants of complexes specified in the title. In obtaining such values Bjerrum's spectrophotometric method of corresponding solutions was utilized, a method particularly well suited to the investigation of processes involving successive complex formation. It should be observed that this aspect has not always received due consideration in earlier spectrophotometric studies^{6,7}.

The results presented in this paper are intended to constitute part of a comprehensive study of complex stability, including complexes of the mentioned metals with a series of unsubstituted monocarboxylic acids, for which several essentially different methods are being employed^{5,9,10}.

EXPERIMENTAL

Absorbance were measured at constant temperature, $25 \pm 0.1^\circ$ C, with a Unicam SP 500 Quartz Spectrophotometer, using silica cells. All systems investigated had

* Correspondence should be addressed to: Jelena Savić, Institute of Chemistry, Vojvode Putnika 43, 71000 Sarajevo, Yugoslavia.

the same ionic strength of 2, and nearly the same pH-values (lactate solutions with cobalt and copper pH 3.2 ± 0.2 , lactate solutions with nickel had 2.9 ± 0.2 , and all β -hydroxypropionate solutions had pH 3.8 ± 0.2). Absorbances of the same solution, repeatedly measured, were reproducible within ± 0.001 unit, while the reproducibility for two identical solutions prepared at different times lay within ± 0.003 units.

All chemicals were analytically pure, only sodium β -hydroxypropionate (a product from Fluka, Buchs, Switzerland) had the grade *purum*. This salt was recrystallized from water. Its concentration in solutions was ascertained by potentiometric titration with standard sodium hydroxide solution, and checked with a cation exchanger. β -Hydroxypropionate buffer solutions with constant acid-to-salt ratios [1 : 1 for Co(II) and Ni(II); 2 : 1 for Cu(II)] were made up the day they had to be used by adding a sufficient amount of perchloric acid to the salt solution. Lactate buffer solutions (1 : 1) were prepared as described before¹¹. Perchlorates of metals were prepared by adding excess perchloric acid to the respective salts; thus copper perchlorate was prepared from basic copper carbonate, and the perchlorates of cobalt and nickel from their nitrates. The solutions thus obtained were evaporated until all nitric acid and most of the perchloric acid were removed, and the residual perchlorates were recrystallized twice. Metal concentrations in stock solutions were determined by electrolysis¹², while the concentrations of free perchloric acid were estimated potentiometrically; free perchloric acid concentrations had to be allowed for when calculating total ligand concentrations (C_L) in experimental solutions. Ionic strength was adjusted to the specified value by addition of sodium perchlorate.

RESULTS

Experimental conditions and the way in which the method of corresponding solutions is to be applied were described in a previous paper¹⁰.

By inspection of absorbance curves (recorded in the visible range, Figs. 1—3) the wavelengths were selected for subsequent measurements so as to ensure the best possible resolution of metal-ion and metal complex bands. Absorbance measurements were carried out at the following wavelengths: for nickel solutions, 660 nm; for lactate cobalt solutions, 520 nm; for β -hydroxypropionate cobalt solutions, 510 nm; for lactate copper solutions, 790 nm; for β -hydroxypropionate copper solutions, 745 nm. Data for experimental absorbance *vs.* total ligand concentration curves were recorded for three or four different total metal ion concentrations (C_M), selecting proper optical path-lengths (d) in order to satisfy the condition $C_M \cdot d = \text{const}^{13}$. All ligand-free solutions of metal ions obeyed Beer's law. The results of these experiments are shown on Tables I—III.

When absorbances were measured at the specified wavelengths, absorption due to free ligand was usually negligible, except with β -hydroxypropionate systems (Fig. 1). But even in this instance ligand absorption had only to be considered in the range of lowest metal concentrations because of large optical path lengths encountered in this range (*e. g.* $C_M = 10 \text{ mM}$, $d = 40 \text{ mm}$); although the absolute ligand absorption is very slight, a correction of total absorbance values proved necessary. These corrections were made by subtracting the amount of absorbance by an equal ligand concentration from the measured value. Such procedure neglects the influence of metal-bound ligand, but this was believed permissible because of a large ligand excess.

Measurements at higher ligand concentrations in systems containing β -hydroxypropionate copper complexes and lactate complexes of cobalt and nickel were precluded by precipitation occurring at such ligand concentrations. It is likely that the precipitated species were neutral complexes. On the other hand, measurements with lactate complexes had to be limited towards higher ligand concentrations because of deformations arising in experimental curves.

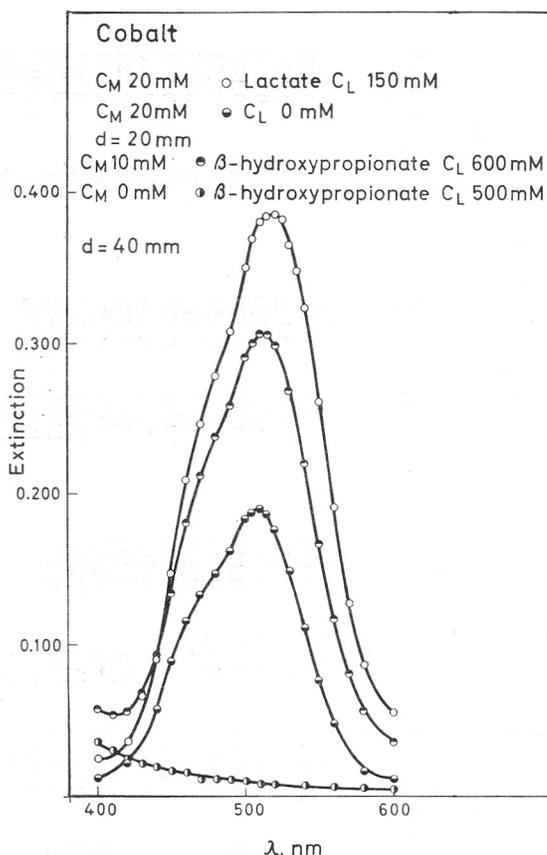


Fig. 1. Light absorption curves of Co(II) solutions.

Absorbance *vs.* total ligand concentration curves served to establish corresponding solutions, *i. e.* solutions exhibiting equal absorbances at different total metal and total ligand concentrations.

Within the limits of experimental error each group of corresponding solutions exhibited a linear C_M *vs.* C_L relationship in the entire range of ligand concentrations employed. These results suggest that no polynuclear complexes were formed in the systems under investigation. Best lines were fitted to the experimental points by the least-square method, and from these lines both the average number of ligands bound (n), and free ligand concentrations ($[L]$) were obtained as slopes and intercepts, respectively. The values for n and $[L]$ were then utilized to determine stability constants by the Fronaeus graphical method¹⁴. These stability constants plus the values of $\log [L]$, n , and C_M were used as input data for executing the Gauss Z program for non-linear least-square refinement calculation according to R. S. Tobias¹⁵. Calculations were carried out with a Gamma 30 digital computer. The program provided for ten refinement cycles of the stability constants.

TABLE I
Cobalt and Nickel Solutions

Cobalt lactate, $\lambda = 520$ nm					Nickel lactate, $\lambda = 660$ nm				
C_M/mM					C_M/mM				
10	20	40	80		20	40	80		
C_L /mM	C_L /mM	C_L /mM	C_L /mM	E d = 5 mm	C_L /mM	C_L /mM	C_L /mM	E d = 20 mm	E d = 10 mm
0.9	0.187	0.4	0.181	0.183	1.2	0.154	1.5	0.151	0.152
1.9	0.189	1.4	0.185	0.188	3.2	0.157	4.5	0.159	0.151
2.9	0.192	2.4	0.186	0.188	6.2	0.166	6.5	0.162	0.151
4.9	0.198	4.4	0.187	0.193	8.2	0.171	11.5	0.169	0.158
7.9	0.208	7.4	0.196	0.202	13.2	0.183	16.5	0.179	0.164
9.9	0.213	9.4	0.197	0.205	18.2	0.196	26.5	0.211	0.175
14.9	0.224	14.4	0.206	0.217	28.2	0.215	36.5	0.223	0.185
19.9	0.233	19.4	0.213	0.228	38.2	0.233	46.5	0.238	0.197
29.9	0.256	29.4	0.245	0.245	48.2	0.249	56.5	0.262	0.206
39.9	0.277	39.4	0.264	0.277	58.2	0.266	76.5	0.286	0.224
49.9	0.294	49.4	0.281	0.282	78.2	0.293	96.5	0.302	0.244
59.9	0.308	59.4	0.275	0.296	98.2	0.312	116.5	0.326	0.258
79.9	0.333	79.4	0.300	0.320	118.2	0.327	146.5	0.344	0.282
99.9	0.359	99.4	0.321	0.342	148.2	0.343	176.5	—	0.307
119.9	0.376	119.4	0.342	0.359	178.2	—	196.5	—	0.319
149.9	0.399	149.4	0.365	0.384	198.2	—	—	—	—
179.9	—	179.4	0.389	0.401	—	—	—	—	—
—	—	—	0.399	0.417	—	—	—	—	—

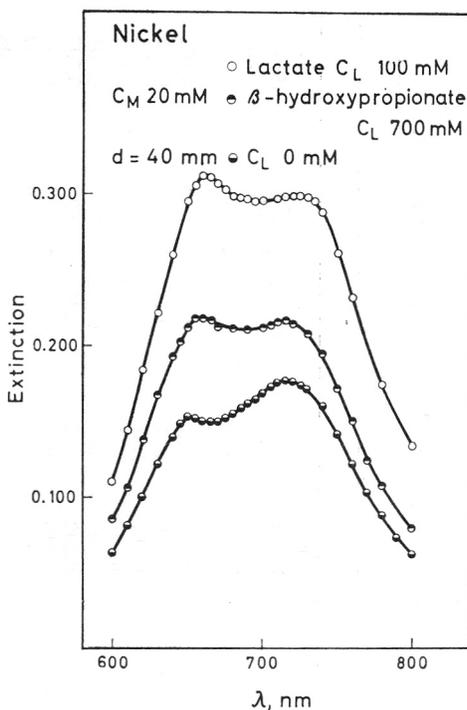


Fig. 2. Light absorption curves of Ni(II) solutions.

Computer output data included the refined stability constants and their standard errors, and calculated formation functions. The values for stability constants obtained by both the graphical and the digital methods are presented on Table IV.

DISCUSSION

The stability constants for lactato complexes reported in this paper, which were determined by the corresponding-solutions spectrophotometric method, are in good accordance with values, obtained by potentiometric, polarographic, and ion-exchange methods, recently reported in the literature²⁻⁵.

Admittedly our constants for lactato complexes of cobalt and nickel are somewhat below, and those for copper somewhat above the literature values. Thus with the lactato cobalt complexes our value for β_1 is 19, while H. Thun *et al.*⁴ obtained 23.4 potentiometrically, and G. Calabro *et al.*^{2,3} give 25.7 as the value determined both potentiometrically and by ion exchange. For lactato complexes of nickel our value of β_1 is 37, compared to 38.9 and 42.5, respectively, as reported by the authors cited. With lactato copper complexes we found $\beta_1 = 431$ by spectrophotometry, and 350 by polarography; the above authors give the values 309 and 316, respectively. Still, if certain differences in the composition of media are accounted for, and especially if the different capacities of methods are considered, we regard these accordances as satisfactory.

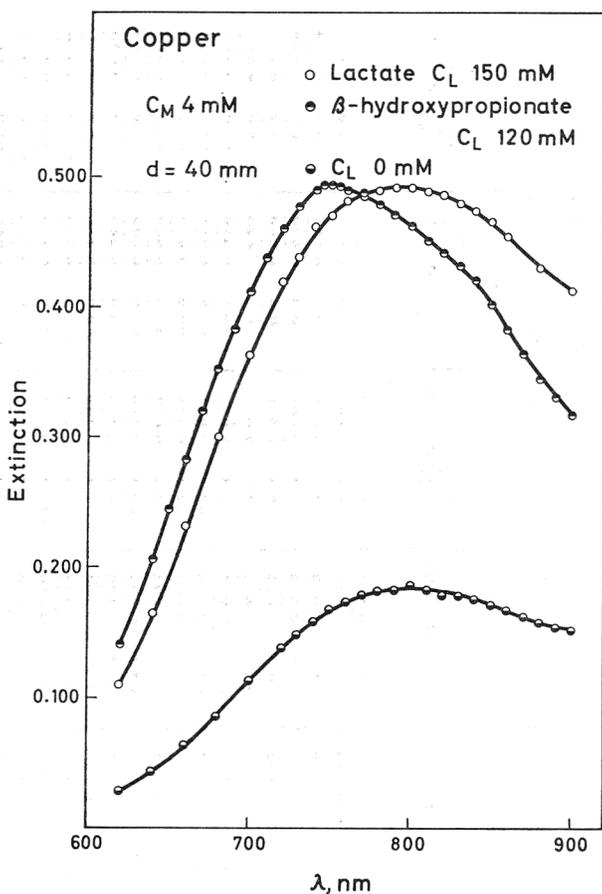


Fig. 3. Light absorption curves of Cu(II) solutions.

However, by using a conductometric method W. P. Evans and C. B. Monk¹ arrived at markedly higher stability constants for the lactato complexes of all three metals, *viz.* to β_1 -values of 79, 164, and 1047, respectively. For the β -hydroxypropionato complexes of copper other authors, M. Lloyd *et al.*⁸, determined $\beta_1 = 832$ (the value extrapolated to zero ionic strength) by the solubility method, but they were working with a different medium.

Strikingly, wide discrepancies between stability constant values are found throughout in spectrophotometric work. Thus M. Bobtelsky and I. Bar-Gadda⁶ obtained β_2 -values 48 and 501, respectively, for lactato cobalt and lactato copper complexes using Job's method. Employing the Asmus and the McConnell-Davidson methods, S. Ramamoorthy and M. Santrappa⁷ were led to β_1 values 126 and 102, respectively, for lactato copper complexes, while for the β -hydroxypropionato copper complex these methods gave β_1 's 501 and 363, respectively, and the Dey-Mukerji method gave $\beta_1 = 3987$. It is quite obvious that these discrepancies must be primarily attributed to inadequacies of some

TABLE III
 Copper Solutions

Lactate, $\lambda = 790$ nm					β -hydroxypropionate, $\lambda = 745$ nm					
C_M/mM					C_M/mM					
4	8	16	32	E	4	8	16	32	E	
C_L/mM	C_L/mM	C_L/mM	C_L/mM	$d = 5$	C_L/mM	C_L/mM	C_L/mM	C_L/mM	C_L/mM	$d = 5$
1.7	1.4	0.209	—	—	1.7	1.4	0.178	—	—	—
2.7	2.4	0.225	0.5	0.190	2.7	2.4	0.187	1.8	0.177	0.5
4.7	4.4	0.251	2.5	0.202	4.7	4.4	0.202	3.8	0.191	2.5
7.7	7.4	0.286	5.5	0.218	7.7	7.4	0.227	6.8	0.206	5.5
9.7	9.4	0.296	7.5	0.223	9.7	9.4	0.239	8.8	0.223	7.5
14.7	14.4	0.332	12.5	0.248	14.7	14.4	0.270	13.8	0.249	12.5
19.7	19.4	0.357	17.5	0.263	19.7	19.4	0.297	18.8	0.273	17.5
29.7	29.4	0.390	27.5	0.303	29.7	29.4	0.341	28.8	0.311	27.5
39.7	39.4	0.410	37.5	0.333	39.7	39.4	0.371	38.8	0.345	37.5
49.7	49.4	0.421	47.5	0.358	49.7	49.4	0.394	48.8	0.369	47.5
59.7	59.4	0.433	57.5	0.380	59.7	59.4	0.412	58.8	0.393	57.5
79.7	79.4	0.449	77.5	0.409	79.7	79.4	0.440	78.8	0.423	77.5
99.7	99.4	0.462	97.5	0.428	99.7	99.4	0.465	98.8	0.449	97.5
119.7	119.4	0.470	117.5	0.442	119.7	119.4	0.484	118.8	0.468	117.5
149.7	149.4	0.481	147.5	0.458	149.7	149.4	0.502	148.8	0.483	147.5
179.7	179.4	—	177.5	0.474	179.7	179.4	0.518	178.8	0.510	177.5
199.7	199.4	—	197.5	0.479	199.7	199.4	—	198.8	0.520	197.5

TABLE IV
Stability Constants (\pm standard errors)

Ligand	Metal	β_1		β_2		β_3	
		graph.	comp.	graph.	comp.	graph.	comp.
Lactate	Co ²⁺	23	19 \pm 1	309	337 \pm 7		
	Ni ²⁺	39	37 \pm 2	853	868 \pm 19		
	Cu ²⁺	360	431 \pm 21	14 \times 10 ³	(12.68 \pm 1.02) \times 10 ³	16.1 \times 10 ⁴	(18.83 \pm 1.06) \times 10 ⁴
β -hydroxy-propionate	Co ²⁺	2.9	3.1 \pm 0.1				
	Ni ²⁺	7.5	6.0 \pm 0.4	19	21 \pm 1		
	Cu ²⁺	67	58 \pm 3	1582	1609 \pm 42		

of the spectrophotometric method when used for systems capable of successive complex formation, as well as to differences in the handling of data.

Anyway, the stability constants presented in this paper indicate that the investigated complexes obey the natural order of stability given by Irving and Williams¹⁶ viz. $\text{Co} < \text{Ni} < \text{Cu}$.

Similarly as with other monocarboxylate complexes of cobalt, nickel, and copper^{5,9,10} the stabilities of copper complexes with either ligand greatly exceed those of the cobalt and nickel complexes, a relationship that can be explained by the stabilizing Jahn-Teller effect.

The relative basicities of ligand would suggest a greater stability for β -hydroxypropionato complexes, and a smaller stability for lactato complexes. Since this expectation is not fulfilled by the relationship of the stability constants it seems obvious that lactato complexes are stabilized by chelate ring formation: their fivemembered chelate rings are well known to be the most stable kind of rings formed by saturated ligands.¹⁷ Conversely, the low stability of β -hydroxypropionato complexes, comparable in magnitude to the stabilities of acetato, propionato, and butyrato complexes⁹, indicates that the effect of chelate ring formation in β -hydroxypropionato complexes is either very small, or altogether lacking.

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IZVOD**Spektrofotometrijsko određivanje konstanta stabilnosti laktato-
i β -hidroksipropionato-kompleksa kobalta(II), nikla(II) i bakra(II)***J. Savić, M. Savić i I. Filipović*

Određene su konstante stabilnosti laktatnih i β -hidroksipropionatnih kompleksa Co(II), Ni(II) i Cu(II) primjenom spektrofotometrijske metode korespondentnih otopina po Bjerrumu. Istraživanja su vršena u vidljivom području spektra. Konstante stabilnosti prisutnih kompleksa procijenjene su grafičkom metodom S. Fronaeusa. Ovako dobivene vrijednosti poslužile su kao osnova za izračunavanje konstanti stabilnosti i odgovarajućih standardnih pogrešaka pomoću digitalnog elektroničkog računala, koristeći Gauss Z program prema R. S. Tobiasu.

KEMIJSKI INSTITUT UNIVERZITETA
U SARAJEVU

I

INSTITUT ZA ANORGANSKU I ANALITIČKU
KEMIJU SVEUČILIŠTA U ZAGREBU

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