

Spectrophotometric and Potentiometric Determination of Stability Constants of 2,3-Dihydroxypropionato Complexes of Cobalt(II), Nickel(II) and Copper(II)

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Stability constants of 2,3-dihydroxypropionato complexes of cobalt(II), nickel(II) and copper(II) were obtained from spectrophotometric and potentiometric data. Spectrophotometric measurements were made in the visible region using Bjerrum's method of corresponding solutions. The change of concentration of hydrogen ions in carboxylate buffers has been measured by potentiometric titration. The stability constants and their 95 per cent confidence intervals were calculated by a digital computer. On the basis of the obtained results the stability of the investigated complexes is discussed with respect to the ligand basicity and the presence of the hydroxyl groups within the ligand molecule.

Previous investigations reported the stability of some metal ion complexes with certain monohydroxy substituted monocarboxylic acid ions obtained by different methods¹⁻⁶. These investigations were performed to give some insight into the correlation between the stability of the monohydroxy substituted monocarboxylate complexes and the nature of the central metal ion, the basicity of the ligand and the position of the hydroxyl group substitution. In continuation of a systematic investigation of metal complexes with hydroxymonocarboxylate ions, this paper describes the results obtained in a study of complexes specified in the title. So far only a few papers have dealt with stabilities of 2,3-dihydroxypropionate complexes^{7,8}. No data are reported in the literature for 2,3-dihydroxypropionate complexes of cobalt(II), nickel(II) and copper(II). The results presented in this paper are intended to give some insight into the relationships of the stability of the complexes mentioned with respect to the donor properties of 2,3-dihydroxypropionate ion.

EXPERIMENTAL

Sodium 2,3-dihydroxypropionate was prepared from commercially available 2,3-dihydroxypropionic acid (glyceric acid) (66 per cent, Fluka) by neutralization with p. a. sodium hydroxide, which was added in excess in order to destroy the associated forms of glyceric acid. The solution was purified by filtration with charcoal, activated GR. Excess sodium hydroxide was removed by passing purified CO₂ through the solution for several hours. Ethanol was then added to the solution

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until the precipitation of sodium hydrogencarbonate together with coprecipitation of impurities from glyceric acid began. The filtrate was heated under reduced pressure and the solid residue was dissolved in a small amount of water. The solution was treated again with CO_2 and ethanol and the filtrate was heated under reduced pressure. This procedure was repeated twice. The sodium salt of glyceric acid finally obtained contained small amounts of sodium hydrogencarbonate and sodium carbonate which were determined by potentiometric titration with perchloric acid. The total concentration of sodium ion was determined by potentiometric titration with perchloric acid in glacial acetic acid. The concentration of sodium 2,3-dihydroxypropionate was determined as the difference in both titrations.

Buffer solutions were prepared by adding perchloric acid to sodium 2,3-dihydroxypropionate solution. The concentration of sodium 2,3-dihydroxypropionate in buffer solution was determined by potentiometric titration of a solution with sodium acetate in the presence of known excess of perchloric acid. The titration was performed in glacial acetic acid medium.

Cobalt(II) and nickel(II) perchlorates were prepared from corresponding carbonates, copper(II) perchlorate from copper(II) oxide and perchloric acid, and recrystallized twice. The concentration of metal ions was determined by potentiometric chelatometric titration. Constant ionic strength was obtained by adding sodium perchlorate.

RESULTS

Spectrophotometric investigation

Absorption spectra of Co(II), Ni(II) and Cu(II) 2,3-dihydroxypropionate complexes at various ligand concentrations were recorded with a Beckman Acta III spectrophotometer. From these spectra (Fig. 1) it can be seen that, at wavelengths of 520, 670 and 760 nm, the increase of absorbance due to formation of Co(II), Ni(II) and Cu(II) 2,3-dihydroxypropionate complexes, respectively, is largest.

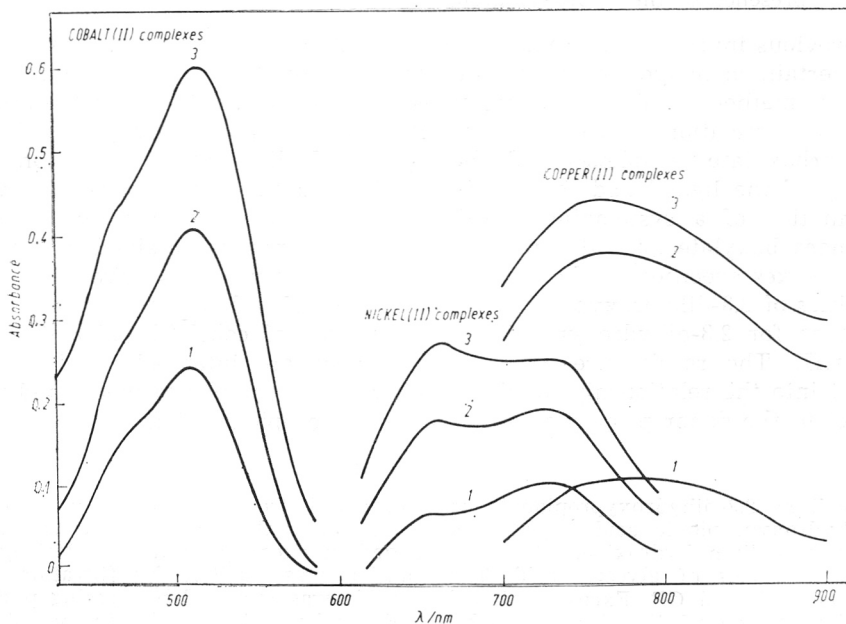


Fig. 1 Absorption spectra of Co(II), Ni(II) and Cu(II) 2,3-dihydroxypropionate complexes. $d = 3$ cm; $C_M = 0.20, 0.25$ and 0.05 mol dm^{-3} of Co(II), Ni(II) and Cu(II), respectively; $C_L = 0.0(1), 0.1(2)$ and $0.3(3)$ mol dm^{-3}

For the determination of composition and stability constants of these complexes Bjerrum's method of corresponding solutions⁹ was used in the same manner as described in one of our previous papers¹⁰. At selected wavelengths the absorbance as a function of total ligand concentration, C_L , in the buffer solution with an acid-to-salt ratio of 1:1, was measured at constant temperature (298.2 ± 0.5 K), at constant ionic strength (2 mol dm^{-3} adjusted by addition of NaClO_4) and at two different constant metal ion concentrations, C_M' and C_M'' . In such a way one obtains two absorbance *vs.* C_L curves for each investigated system. One for metal ion concentration C_M' in a spectrophotometric cell of thickness $d' = 2$ cm and the other for metal ion concentration C_M'' in cell of thickness $d'' = 0.2$ cm. In order to satisfy the required condition that $C_M' \cdot d' = C_M'' \cdot d''$ it follows that $10 \cdot C_M' = C_M''$. The concentrations of metal ions C_M'' were 0.2, 0.25 and 0.05 mol dm^{-3} for Co(II), Ni(II) and Cu(II), respectively.

The above functions measured with a Carl Zeiss VSU 1 spectrophotometer in a cell adapted to meet our purpose are given in Fig. 2. The solutions for measurement were prepared directly in the spectrophotometric cell by the procedure outlined previously¹⁰. Additions of solutions were made with a

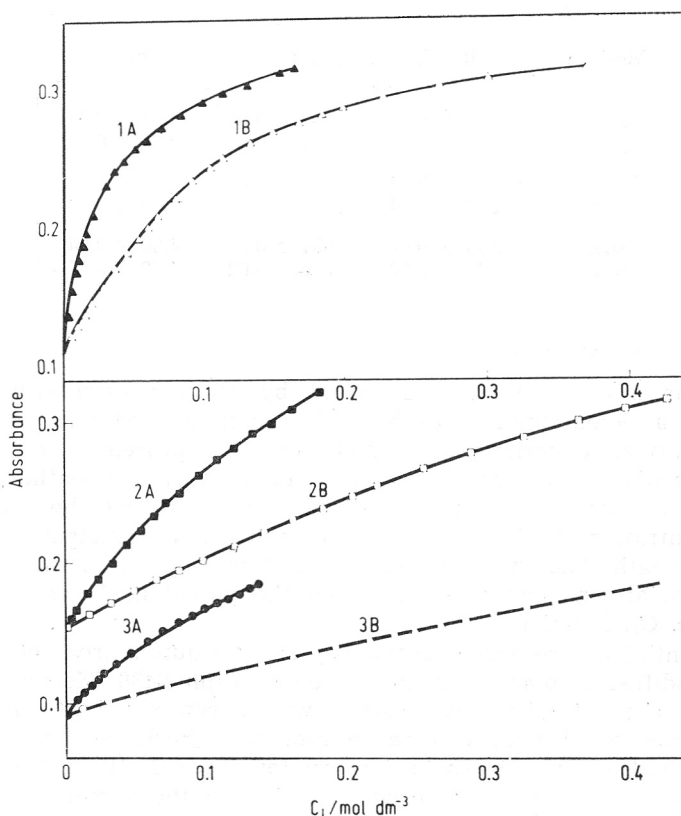


Fig. 2 Absorbance as a function of C_L at constant $C_M \cdot d$ for 2,3-dihydroxypropionato complexes. (1) Cu(II) complexes; (2) Co(II) complexes; (3) Ni(II) complexes; (A) $d' = 2$ cm; $C_M' = 0.020, 0.025$ and $0.005 \text{ mol dm}^{-3}$ of Co(II), Ni(II) and Cu(II), respectively; (B) $d'' = 0.2$ cm; $C_M'' = 0.20, 0.25$ and 0.05 mol dm^{-3} of Co(II), Ni(II) and Cu(II), respectively.

microburet having a reproducibility of 0.001 cm^3 . Each solution was prepared and recorded in duplicate and the mean values are given in Fig. 2. The reproducibility of each measurement within all investigated absorbance ranges were better than $\pm 0.003 \text{ A}$.

From the results given in Fig. 2 by using a computer program described earlier¹⁰, the average number, \bar{n} , of ligands bound to the central metal ion and the free ligand concentration, $[L]$, can be obtained from the corresponding solutions principle. The same computer program was then used to obtain, by numerical interpretation of Fronaeus' method¹¹, the well-known function $F_0 = 1 + \sum_{i=1}^n \beta_i [L]^i$ related to the stability constants, β_i , of the complex species present in the solution. Finally, the computer approach to weighted least squares fitting of F_0 polynomials gives the stability constants and their 95 per cent confidence intervals. These values are given in Table I.

TABLE I
Stability Constants of 2,3-Dihydroxypropionato Complexes at $I = 2 \text{ mol dm}^{-3}$
(NaClO_4)

Metal ion	Method	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
Co^{2+}	spe.	1.18 ± 0.04	1.52 ± 0.08	2.54 ± 0.04	
	pot.	1.30 ± 0.04	1.74 ± 0.04	2.84 ± 0.02	
Ni^{2+}	spe.	1.32 ± 0.04	2.28 ± 0.02		
	pot.	1.46 ± 0.04	2.24 ± 0.02	3.00 ± 0.04	
Cu^{2+}	spe.	2.27 ± 0.04	3.51 ± 0.06	4.80 ± 0.04	
	pot.	2.18 ± 0.02	3.82 ± 0.02	4.62 ± 0.10	5.99 ± 0.02

Potentiometric investigation

The same systems were investigated by another essentially different method, *i. e.* a potentiometric method. The method used was proposed by Fronaeus¹¹ and an experimental arrangement and procedure were outlined in a previous paper¹². The method consists of measuring potential, E_0 , of the buffer solution with a constant acid-to-salt ratio varying the salt *i. e.* the ligand concentration, against the reference solution at constant temperature and ionic strength. The same procedure was then applied in the presence of a constant metal ion concentration giving the potential, E , *vs.* total ligand concentration, C_L , function.

The potential was recorded continuously using a quinhydrone electrode and a slightly modified automated titrator (Potentiograph E436, Metrohm) to meet our purpose. The potential was recorded with a reproducibility of $\pm 0.2 \text{ mV}$ while the reproducibility of volume addition was $\pm 0.01 \text{ cm}^3$. No interaction between quinhydrone and the metal ion was found for Co(II) , Ni(II) and Cu(II) , because the experimentally measured potentials in the presence of different metal ion concentrations for varying hydrogen ion concentrations agreed with that calculated from the Nernst equation within the reproducibility limits of our measurements.

From the measured potentials E_o and E it is easy to calculate the concentration of hydrogen ion in absence of complex formation, $[H^+]_o$, and in presence of complex formation, $[H^+]$, at various total ligand concentrations, C_L . From these values the free ligand concentration, $[L]$, can be calculated from the relationship

$$[L] = \exp \left[\ln \frac{(C_L + [H^+]_o)(C_{HL} - [H^+])}{(C_{HL} - [H^+]_o)} - \frac{E_L}{59.14 \text{ V}} \right]$$

and the average number, \bar{n} , of ligand bound to one central metal ion

$$\bar{n} = \frac{C_L + [H^+] - [L]}{C_M}$$

where C_M and C_{HL} are the total ion and protonated ligand concentrations and $E_L = E_o - E$. Measurements were performed at a temperature of 298.2 ± 0.1 K and at ionic strength of 2 mol dm^{-3} (adjusted by addition of NaClO_4). The constant acid-to-salt ratio was 1 : 1. 2,3-Dihydroxypropionato complexes of Cu(II) were investigated at an acid-to-salt ratio of 3 : 1, as well. Constant metal ion concentrations for Co(II) and Ni(II) were 50 and 100 mmol dm^{-3} , while for Cu(II) it was 10 mmol dm^{-3} . Good agreement between the formation curves for different acid-to-salt ratios excludes the presence of hydroxo complexes, while such agreement for two different metal ion concentrations excludes the presence of polynuclear complexes.

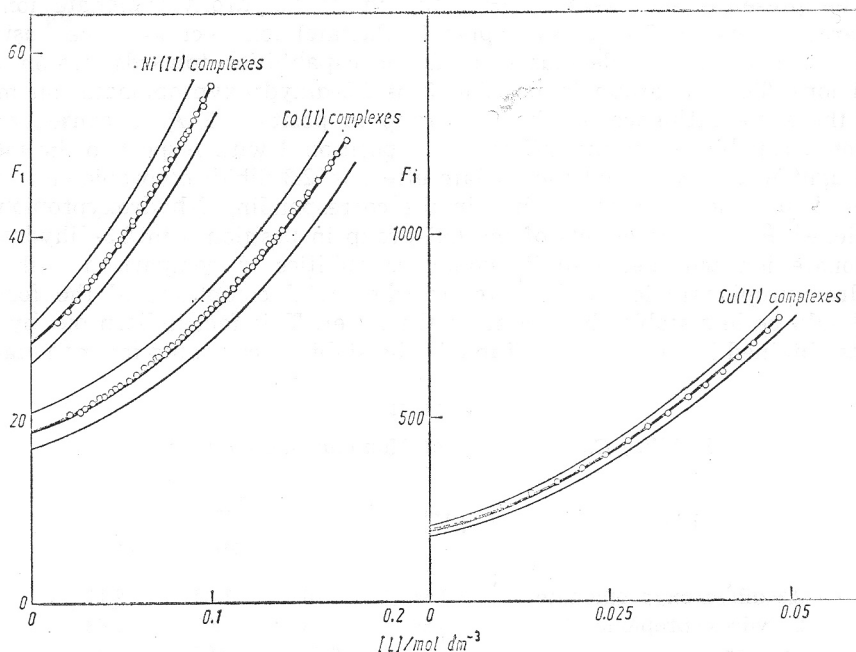


Fig. 3 Potentiometrically determined experimental points of F_1 functions of Co(II), Ni(II) and Cu(II) 2,3-dihydroxypropionato complexes together with theoretical F_1 functions and their 95 per cent confidence intervals calculated by using the final set of stability constants.

A computer program¹² was used for the calculation of \bar{n} and $[L]$ values together with the dissociation constant of protonated ligand, as well as for the evaluation of F_0 polynomials from these values. Furthermore, from the F_0 polynomials, with the same subroutine as used in the spectrophotometric treatment the stability constants and 95 per cent confidence intervals were obtained. These values are also given in Table I. Graphical presentation of the F_1 function ($F_1 = (F_0 - 1)/[L] = \beta_1 + \sum_{i=2}^n \beta_i [L]^{i-1}$), which extrapolation to $[L] = 0 \text{ mol dm}^{-3}$ yields the approximate β_1 values, are given in Fig. 3.

DISCUSSION

From the results given in Table I it can be seen that the stability constants obtained by both methods differ slightly when comparing their 95 per cent confidence intervals. This fact may be due to an influence of the weighting procedure on the error estimates. Besides, some factor inherent in either spectrophotometric or potentiometric method may also have an influence on the difference between the two sets of stability constants. However, both sets agree well within approximately ± 0.1 log units. Such agreement is good taking into account that two different methods are used.

From the values of the first stability constants (β_1), considered in the literature as a criterion in comparing the stabilities of complexes, one can see that the stability of the investigated monoligand complexes obeys as in all previously investigated systems,¹⁻⁶ the well-known order of stability, *i. e.* $\text{Co} < \text{Ni} < \text{Cu}$.

The presence of a second OH-group in 2,3-dihydroxypropionate ion as compared to one in 2-hydroxypropionate (lactate) ion decreases the basicity of the former ion *i. e.* decreases its donor capabilities towards proton and metal ions. The OH-group in position 3 of 2,3-dihydroxypropionate ion must have the same influence on the OH-group in position 2. As a consequence, the donor capabilities of the OH-group in position 2 with respect to the metal ions ought to decrease, and the chelate effect in 2,3-dihydroxypropionate complexes should then be smaller than in the corresponding 2-hydroxypropionate complexes. Both these effects of the OH-group in position 3 in 2,3-dihydroxypropionate ion will decrease its donor capabilities in comparison with the 2-hydroxypropionate ion and, therefore, the metal complexes of the former ion should be less stable than those of the latter. This fact is born out by the results obtained in this work. In Table II the stability constants for monoligand

TABLE II
Stability Constants (β_1) of Monoligand Complexes

Ligand	pK_A^a	$\log \beta_1$		
		Co^{2+}	Ni^{2+}	Cu^{2+}
2,3-dihydroxypropionate	3.54	1.18	1.32	2.17
2-hydroxypropionate ²	3.86	1.28	1.57	2.63
propionate ¹	4.87	0.78	0.86	1.94 ^b

^a Our results, E.m.f. method with quinhydrone electrode, ionic strength 2 mol dm^{-3} (NaClO_4)

^b Unpublished result.

complexes (β_1) of 2,3-dihydroxypropionate, 2-hydroxypropionate and propionate of investigated metal ions are given for comparison. This Table also gives the pK_A values of the corresponding acids, characterizing the ligand basicities. The results in Table II were obtained by the spectrophotometric method, but the same holds true for the results obtained by the potentiometric method.

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REFERENCES

1. I. Filipović, T. Matusinović, B. Mayer, I. Piljac, B. Bach-Dragutinović, and A. Bujak, *Croat. Chem. Acta* **42** (1970) 541.
2. J. Savić, M. Savić, and I. Filipović, *Croat. Chem. Acta* **44** (1972) 305.
3. S. Nushi, I. Piljac, B. Grabarić, and I. Filipović, *Croat. Chem. Acta* **45** (1973) 453.
4. I. Filipović, I. Piljac, B. Bach-Dragutinović, I. Kruhac, and B. Grabarić, *Croat. Chem. Acta* **45** (1973) 447.
5. B. Grabarić, B. Mayer, I. Piljac, and I. Filipović, *J. Inorg. Nucl. Chem.* **36** (1974) 3809.
6. I. Filipović, I. Piljac, B. Grabarić and B. Mayer, *Anal. Chim. Acta*, **76** (1975) 224.
7. L. G. Sillen and A. E. Martell, *Stability Constants*, The Chemical Society, London 1964. — Supplement No 1. The Chemical Society, London 1971.
8. B. Topuzovski and I. Filipović, *Croat. Chem. Acta* **40** (1968) 257.
9. J. Bjerrum, *Kgl. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **21** (1944).
10. B. Grabarić, I. Piljac, and I. Filipović, *Anal. Chem.* **45** (1973) 1932.
11. S. Fronaeus, *Acta Chem. Scand.* **4** (1950) 72.
12. B. Grabarić, B. Mayer, I. Piljac, and I. Filipović, *Electrochim. Acta* **20** (1974), in press.

SAŽETAK

Spektrofotometrijsko i potenciometrijsko određivanje konstante stabilnosti 2,3-dihidroksipropionato-kompleksa kobalta(II), nikla(II) i bakra(II)

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Konstante stabilnosti 2,3-dihidroksipropionato-kompleksa kobalta(II), nikla(II) i bakra(II) određene su spektrofotometrijskom i potenciometrijskom metodom. Spektrofotometrijska mjerenja izvršena su u vidljivom spektralnom području primjenom Bjerrumove metode odgovarajućih otopina. Kod potenciometrijske titracije praćena je promjena koncentracije vodikovih iona u karboksilatnom puferu. Konstante stabilnosti i njihovi 95-postotni intervali pouzdanosti izračunane su s pomoću elektroničkog računala. Na osnovi dobivenih rezultata diskutirana je stabilnost istraživanih kompleksa s obzirom na bazičnost liganda i prisutnost hidroksilnih skupina u molekuli liganda.

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