

CCA-1573

YU ISSN 0011-1643

UDC 546.3

Note

Stability Constants Determination of Mandelate Complexes of Cobalt(II), Nickel(II) and Zinc(II)

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Received May 11, 1985

Stability constants of mandelate (2-phenyl-2-hydroxyacetate) complexes of cobalt(II), nickel(II) and zinc(II) were determined potentiometrically using glass and quinhydrone electrodes at $25.0 \pm 0.1^\circ\text{C}$ and ionic strength 2 mole dm^{-3} (sodium perchlorate). The numerical values of stability constants were evaluated from experimental data by a computer program based on a weighted least squares method.

Determination of the composition and stability of metal-ion mandelate complexes was performed as a part of systematic investigations of unsubstituted and substituted metal-ion monocarboxylate complexes in our laboratory. The intention was to give some insight into factors governing the stability of these complexes¹. In order to complete this study the same experimental conditions (i. e. temperature and ionic strength) have been maintained in the present potentiometric investigations of the above mentioned complexes.

EXPERIMENTAL

Potentiometric measurements were performed with potentiograph Metrohm E436 using a glass electrode (Metrohm EA 109) and a quinhydrone electrode. Volume addition reproducibility was $\pm 0.001 \text{ cm}^3$ and potential reproducibility was $\pm 0.2 \text{ mV}$. Solutions were purged with purified nitrogen for 15 min before the measurements. Reagent addition took approx. 30 min; and during this time nitrogen was passed over the surface of the solution which was stirred magnetically.

All determinations were carried out at $25.0 \pm 0.1^\circ\text{C}$ and at ionic strength 2 mole dm^{-3} (sodium perchlorate).

Each system was studied at two metal-ion concentrations, both of these at two acid-to-salt ratios 1 : 1 and 1 : 2. Concentrations of Co(II) and Ni(II) were 20 and 10 mmole dm^{-3} and of Zn(II) 10 and 5 mmole dm^{-3} . The total ligand concentration was up to 100 mmole dm^{-3} , because at higher ligand concentration precipitation occurred.

Cobalt(II) and nickel(II) perchlorates were prepared from perchloric acid and the corresponding carbonates, while zinc(II) perchlorate was prepared from the corresponding oxide and perchloric acid. All salts were recrystallized three times. Metal-ion concentrations in the stock solutions were determined by complexometric potentiometric titration with a mercury indicator electrode³. Concentrations of free acid in metal perchlorates were also determined and taken into account when pre-

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paring the buffer solution. Analytical grade dl-mandelic acid (Merck), sodium perchlorate and sodium hydroxide were prepared by dilution of corresponding stock solutions.

RESULTS AND DISCUSSION

Experimental data were treated with precision of 10.5 significant digits on the PDP-8 computer programmed to calculate average number, n , of ligand bound to the central metal-ion, the free-ligand concentrations, $[L]$, and the values of the function

$$F_0([L]) = 1 + \sum_{i=1}^N \beta_i [L]^i$$

A weighted least-squares procedure was then used to evaluate the stability constants². Logarithmic values of stability constants are listed in Table I.

TABLE I

Stability Constants of Mandelate Complexes $t = 25^\circ\text{C}$, $I = 2 \text{ mol dm}^{-3}$ (NaClO_4)

Metal ion	Method	$\log K_1$	$\log \beta_2$
Co^{2+}	Pot. (GE)*	1.19 ± 0.01	2.07 ± 0.01
	Pot. (QE)**	1.26 ± 0.01	1.95 ± 0.01
Ni^{2+}	Pot. (GE)	1.31 ± 0.01	2.48 ± 0.01
	Pot. (QE)	1.35 ± 0.01	2.40 ± 0.01
Zn^{2+}	Pot. (GE)	1.36 ± 0.01	2.58 ± 0.01
	Pot. (QE)	1.40 ± 0.01	2.45 ± 0.01

* GE 1 Glass electrode

** QE Quinhydrone electrode

$\text{p}K_A = 3.33$ (our value)

A good agreement between the formation curves² obtained for different metal-ion concentrations and acid-to-salt ratios eliminates the existence of polynuclear complexes, and rules out the existence of hydroxy complexes.

The behaviour of glass and quinhydrone electrodes during potentiometric complex formation measurements was investigated earlier⁷. It was shown that a difference in $\log K_1$ of approximately 0.05 was obtained and that monoligand, stability constants obtained by the glass electrode were always lower than those obtained by the quinhydrone electrode. It was demonstrated that this difference can be attributed to deviation from the Nernst equation. The potential measured with the quinhydrone electrode was higher while the potential measured with the glass electrode was lower than the value calculated from the Nernst equation.

The standard error values in Table I of 0.01 logarithmic units express inner consistency of the measured data. An attempt was made to estimate a realistic error in stability constants determination. All potentials were measured to ± 0.2 mV so the set of data was changed by 0.4 mV and with these new values of potentials a new set of stability constants was calculated. Then an error was assumed in ligand concentration of 10 per cent and in metal ion concentration of 5 per cent. All these changes did not give a greater difference in $\log 1$ of 0.03, which proves that the design of the experimental method is

very good because the stability constants are obtained from the difference in potential measured for the solution of ligand in the presence and absence of metal ion-complex formation. Most errors are canceled through this difference. Therefore, it can be estimated that all the results presented in Table I are realistically confident to ± 0.03 logarithmic units.

On the basis of the stability constants of monoligand complexes, the stability of the investigated systems follows the order Co Ni Zn, which is the same order as stated in this laboratory for all other unsubstituted and substituted monocarboxylate complexes¹.

Lower stability of mandelate complexes of investigated bivalent metal-ions in comparison with the stability of the corresponding glycolate complexes is in accordance with the lower basicity of mandelate ligand (pK_A 3.33) due to the inductive effect of C_6H_5 -group. The stability of the metal-ion complex is lower in the same proportion as that of the proton complex i. e. the contribution to the stability due to chelate coordination of OH-group is approximately one logarithmic unit, which is the same as in glycolate complexes¹ where the chelate coordination was proved by IR in investigations⁵. The same was determined for the investigated mandelate complexes by IR studies of P. V. Khadikar et al.⁶ This points to the conclusion that the inductive effect of C_6H_5 -group in the investigated ligand is independent of the central ion.

The values of monoligand stability constants obtained in our investigations are in good agreement with Folkesson and Larsson's data⁴.

It should be mentioned, however, that these authors investigated the system within a broader ligand concentration range (up to 0.16 mol dm^{-3}) and that they also encountered the precipitation of the complexes from the solution, which prevented the investigation at a higher ligand concentration. In our experience, by using the analytical grade dl-mandelic acid (Merck) it was not possible to prepare the investigated complexes in solution with more than 0.10 mol dm^{-3} of ligand concentration, because at higher concentrations precipitation occurred immediately. In our experiments and in those of Folkesson and Larsson approximately the same metal ion concentrations were used. This is probably the reason why monoligand stability constants are in good agreement between the results presented in this paper and those presented in Folkesson's and Larsson's paper. Biligand stability constants are in fair agreement and we were not able to detect the existence of the third complex in solution within our experimental conditions.

Acknowledgement — The authors are indebted to the Scientific Research Council of Croatia for financial support.

REFERENCES

1. I. Filipović, *Kem. ind.* **30** (1981) 369.
2. B. Grabarić, B. Mayer, I. Piljac, and I. Filipović, *Electrochim. Acta* **20** (1975) 799.
3. G. Schwarzenbach, *Die Komplexometrische Titration*, F. Enke, Stuttgart, 1960.
4. B. Folkesson and R. Larsson, *Acta Chem. Scand.* **22** (1968) 1953.
5. R. Larsson, *Acta Chem. Scand.* **19** (1965) 783.
6. P. V. Khadikar, R. L. Ameria, M. G. Kekre, and S. D. Chauhan, *J. Inorg. Nucl. Chem.* **35** (1973) 4301.
7. I. Kruhac and I. Filipović, *Croat. Chem. Acta* **52** (1979) 207.

SAŽETAK

Istraživanje stabilnosti mandelato-kompleksa kobalta(II), nikla(II) i cinka(II)

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Konstante stabilnosti mandelato-kompleksa kobalta(II), nikla(II), i cinka(II) određene su potencijometrijskom titracijom u tamponskim otopinama stalne ionske jakosti 2 mol dm^{-3} (NaClO_4).