EQUILIBRIUM CORRELATIONS OF COMPLEXES OF Co(II), Cu(II), Hg(II), Cd(II) AND Mn(II) WITH CIS-2-AMINO-CYCLOHEXANE-CARBONIC ACID

By

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The successive equilibrium constants of complexes of cis-2-amino-cyclohexane-carbonic acid with Co(II), Cu(II), Mn(II), Hg(II) and Cd(II)-ions have been determined. It was stated that in the case of transition metal ions the logarithms of stability constants increase with the growth of the atomic number and ionization potential.

Introduction

Equilibrium correlations prevailing among different amino acids and metal ions in aqueous solutions have been discussed in a great number of papers since BJERRUM's first investigation [1]. Investigation of these correlations is not only of theoretical but also of biochemical interest, since in the case of most enzymes and proteins metal ions are found to be linked with amino acids.

Experimental

Apparatus and chemicals employed: The pH-metric titrations were carried out by using a Radelkisz titriscope Model OP 205. Accuracy of the pH-measurements was ± 0.01 pH. Temperature was kept constant within ± 0.2 C° by means of a Höpler ultra-thermostat. The stock-solutions containing the Co(II), Cu(II), Hg(II), Cd(II) and Mn(II)-ions were prepared of the corresponding p.a. metal-nitrates. The cis-2-amino-cyclohexane-carbonic-acid was prepared according to [2] and recrystallized by using aqueous-acetone mixture; Mp. 231 C°. The ionic strength was adjusted to 0,1 by KNO_3 solution. For the pH-metric titrations 0,1 M and 0,2 M NaOH, and 0,1 M HCl solutions were used.

Titration: Solutions of metal(II)-ion and cis-2-amino-cyclohexane-carbonic acid of $2 \cdot 10^{-3}$ M and 10^{-2} M concentrations, respectively, have been titrated, the ionic strength was adjusted to 0,1. For the determination of the dissociation constants 10^{-2} M cis-2-amino-cyclohexane-carbonic acid was used at 25 C° and $I = 0$ 1.

Calculations: Formation curves were calculated from the titration data according to the relations obtained by ALBERT [3]:

$$\bar{n} = \frac{C_A - [A]\left(1 + \dfrac{[H^+]}{K_{a2}} + \dfrac{[H^+]^2}{K_{a1} K_{a2}}\right)}{C_M} \tag{1}$$

$$A = \frac{C_A - [\text{NaOH}] + [\text{HCl}] - [\text{H}^+] + [\text{OH}^-]}{\dfrac{[\text{H}^+]}{K_{a2}} + 2\dfrac{[\text{H}^+]^2}{K_{a1}K_{a2}}} \qquad (2)$$

In equations (1) and (2) C_A and C_M refer to the total concentrations of the ligand and metal-ions respectively, while the square brackets stand for the equilibrium concentrations. K_{a1} and K_{a2} refer to the acidic and basic dissociation constants of the ligand, $[A]$ to the concentration of the free ligand, while $\bar{n}$ indicates the average coordination number. The formation curves are plotted in Fig. 1.
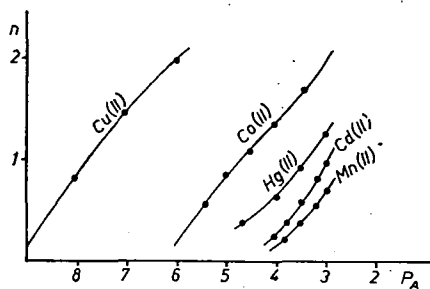
Using data of Fig. 1, the successive constants were calculated graphically according to F. ROSSOTTI and H. ROSSOTTI [4] on the basis of the following equations:

Fig. 1. Formation curves of metal (II)-
-cis-amino-cyclohexane-carbonic acid com
plex systems at 25 C°, I=0,1 (KNO₃).
Metal(II)-ions = $2 \cdot 10^{-3}$ M, cis-2-amino-
cyclohexane-carbonic acid = $1,0 \cdot 10^{-2}$ M

$$n = \frac{\sum_1^N i\beta_i[A]^i}{1 + \sum_1^N \beta_i[A]^i} \qquad (3)$$

Rearranging the equation we obtain

$$\sum_0^N (i - \bar{n})\beta_i[A]^i = 0 \qquad (4)$$

whereof the following equation can be deduced:

$$\frac{\bar{n}}{(1-\bar{n})[A]} = \beta_1 + \beta_2\frac{(2-\bar{n})[A]}{(1-\bar{n})} + \sum_3^N \frac{(N-\bar{n})}{(1-\bar{n})}\beta_n[A]^m \qquad (5)$$

Thus β_1, β_2 and β_3 can be determined with a graphic method using the following equations:

$$\frac{\bar{n}}{(1-\bar{n})[A]} = \beta_1 + \beta_2\frac{(2-\bar{n})[A]}{(1-\bar{n})} + \beta_3\frac{(3-\bar{n})[A]}{(1-\bar{n})} \qquad (6)$$

$$\frac{\bar{n} - (1-\bar{n})\beta_1[A]}{(2-\bar{n})[A]^2} = \beta_2 + \beta_3\frac{(3-\bar{n})[A]}{(2-\bar{n})} \qquad (7)$$

According to equations (6) and (7) values $0 < \bar{n} < 1$ and $1 < \bar{n} < 2$, respectively for the calculations can be used β_3 can be calculated as an ordinate intercept from the following equation:

$$\frac{\beta_1(\bar{n}-1)[A] + \bar{n}}{(3-\bar{n})[A]^3} = \beta_3 + \beta_2\frac{(2-\bar{n})}{(3-\bar{n})} \qquad (8)$$

Results

Dissociation constants of the cis-amino-cyclohexane-carbonic acid resulted to be $P_{k1} = 3,47$ and $P_{k2} = 10,44$. Calculations of the successive equilibrium constants

Table I

Stability constants of complexes of Co(II), Cu(II), Hg(II), Cd(II) and Mn(II)-ions with cis-2-amino-cyclohexane-carbonic acid

	lg k_1	lg k_2	lg k_1/k_2	lg β_2	lg k_3	lg k_2/k_3	lg β_3
Cu(II)	8,62	7,74	0,88	16,36	—	—	—
Co(II)	5,52	4,80	0,72	10,32	3,20	1,60	13,52
Hg(II)	3,68	2,71	0,97	6,39	—	—	—
Cd(II)	3,45	2,65	0,80	6,10	—	—	—
Mn(II)	3,25	2,41	0,84	5,66	—	—	—

were made by using these dissociation constants. Values obtained are listed in Table I.

From Table I it can be seen that, according to their stability, the metal-ions can be put in the following order: Cu > Co > Hg > > Cd > Mn; in the case of transition metals: Cu > Co > Mn. For different ligands, as stated by MELLOR and MOLEY [5, 6], the order of bivalent metal-ions is Pd > Cu > Ni > Pb > Co > Cn > > Zd > Fe > Mn > Mg. According to the view of the authors this order can be explained by the basicity of the metal-ions. The weakly basic Cu and Pd form the most stable complexes, while the most unstable ones are formed by Mn and Mg of strong basic properties.

A relation betwen the atomic number and the logarithm of stability constant was found by IRWING and WILLIAMS [7]. In Fig. 2 lg β_1 and lg β_2 are plotted as functions of the atomic number.

It is obvious that with increasing atomic numbers the stability increases.

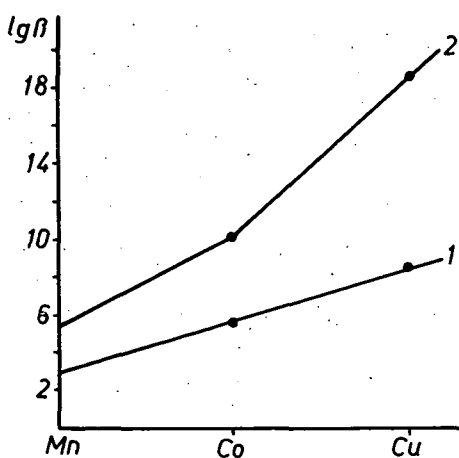In Fig. 3 the logarithms of the stability constants are plotted

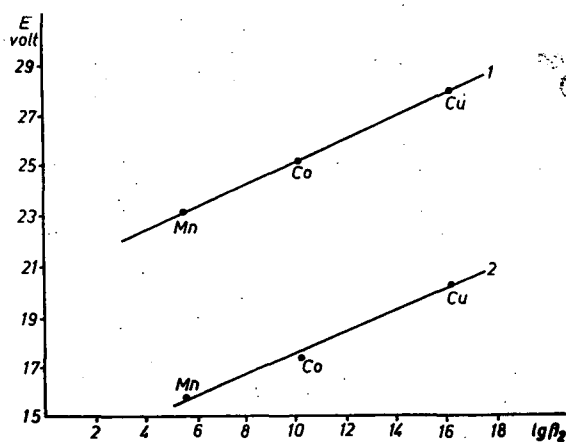Fig. 2. *1*: lg β_1, *2*: lg β_2

Fig. 3. Logarithms of stability constants *versus* (*1*) second ionization potential and (*2*) sum of first and second ionization potential

against the second ionization potential (*1*) and the sum of the first and second ionization potentials (*2*).

During ionization of transition metals the electron splits off from the *d* orbit. Fig. 3 shows that in the case of transition metals the logarithms of stability constants change linearly with ionization potentials. It is to be noted that the increase in the number of 3*d* electrons is the same as if the stability constants increase. Therefore it is likely that in the bond between the metal-ion and the ligand the participation of *d* orbits plays a decisive role.

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РАВНОВЕСНЫЕ СООТНОШЕНИЯ КОМПЛЕКСОВ ИОНОВ
Co(II), Cu(II), Hg(II), Cd(II), Mn(II)
2-АМИНО-ЦИКЛОГЕКСАН-КАРБОННОЙ КИСЛОТОЙ

В. Николашев, Д. Гендеш и Г. Бернат

Авторы рассчитали константы равновесия комплексов 2-амино-циклогексан-карбонной кислоты с ионами·металлов.

Они нашли, что в случае переходных металлов логарифмы константы стабильности увеличиваются с увеличением·атомных номеров и ионизационных потенциалов.