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Stability of Co(II), Ni(II) and Cu(II) Complexes with Methoxyacetic, Phenylacetic and Cyclohexylacetic Acids

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The main aim of these studies was to determine the complexogenic properties of the methoxyacetic, phenylacetic and cyclohexylacetic acids with the Co(II), Ni(II) and Cu(II) ions, *i.e.* determination of created compounds composition, their stability constants and then comparison of the obtained results with the data obtained earlier for complexes of the same metals with the acetic acid [1]. Although the acetic acid complexes with selected 3d-electron metal ions were studied by many authors [2,3], we have considered necessary to carry out the measurements also for this acid in the same conditions and using the same method as in the case of the other studied acids and treating the metal ion – a simple carboxylic acid system as the reference one. Because of weak complexogenic properties of the carboxylate ion, the acetic acid forms with bivalent Co, Ni and Cu ions complexes of low stability. It seemed interesting to check how the presence of ether CH_3–O– group and cyclic substituents: phenyl C_6H_5- and cyclohexyl C_6H_{11}- in the acetic acid would change its complexogenic properties. It should be emphasised, that except for the author's work, in which the stability of the complexes of the cyclohexylacetic acid with the Cu(II) ions was determined [4], there are no literature data on this acid complexes. However, there exist few papers devoted to the complexogenic properties of the methoxy- and phenylacetic acids. They concern yet only the Cu(II) complexes [4–7].

It was interesting to consider this subject not only because of a limited number or complete lack of the literature data. The carboxylic acids studied here and their derivatives and especially the phenylacetic acid are used for example as good extraction agents – thus they can be useful for analytical purposes. They are also used as controllers of plants' growth and therefore their complexogenic properties with Co(II), Ni(II) and Cu(II) – *i.e.* bioactive elements – were studied [8–10].

Compositon and consecutive stability constants of the complexes were determined using two parallel experimental methods: potentiometric titration based on changes in hydrogen ions activity during the complexation reaction [11] and spectrophotometric examination of "corresponding solutions" of Bjerrum [12]. In the potentiometric method each measurement was preceded with the determination of the activity coeffi-

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cients $\overline{f}_H$ of the hydrogen ions for the standard solutions, using the method described in [13]. Then the activity was recalculated into the concentration and the concentration equilibrium constants were determined, also obtained by the spectrophotometric method, because the absorption coefficient is a real parameter and practically does not depend on the ionic environment [14]. Thus, the data obtained by these two methods can be directly compared.

All reagents were of analytical grade. Concentrations of Co(II), Ni(II) and Cu(II) ions were determined complexometrically using EDTA and also electrometrically. Acids were applied in the form of sodium buffers with a ratio of acid to salt concentration such that the pH was in the interval from 3.5 to 4.5. Constant ionic strength of μ = 0.1 was maintained by adding $NaClO_4$. The measurements were carried out at three different concentrations of the central ion. The emf values were read to the nearest 0.2 mV with a Radiometer PHM-220 pehameter with a glass-silver-silver chloride electrodes system. The method used for potentiometry was analogous to that described in [15]. Basing on the obtained formation curves the values of the concentration stability constants were then calculated numerically by the Martell and Motekaitis program [16].The dissiociation constants of the acids studied were determined by measuring hydrogen ion activities at the point of half-neutralization.

Absorbance measurements for the individual systems were performed in the following conditions:

Co(II) – λ = 510 nm, pH = 4.2, $[Co^{2+}]$ = 10 and 25 mM
Ni(II) – λ = 670 nm, pH = 3.9, $[Ni^{2+}]$ = 10 and 25 mM
Cu(II) – λ = 800 nm, pH = 4.1, $[Cu^{2+}]$ = 5 and 12.5 mM

using a VSU-2 (Carl Zeiss, Jena) spectrophotometer and glass cuvettes 2 and 5 cm. The measurements of absorbance were carried out on solutions with increasing ligand concentrations up to the maximum acetic, methoxyacetic and phenylacetic acid concentration of 150 mM. The highest cyclohexylacetic acid concentration was 40 mM, because of its limited solubility. The stability constants were calculated using the numerical scheme developed by Grabarić *et al.* [17].

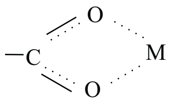
Using the potentiometric and spectrophotometric methods it was shown that three of the studied acids, *i.e.* the methoxyacetic, phenylacetic and acetic acid form two mononuclear complexes of a low stability ML^+ and ML_2 with the Co(II), Ni(II) and Cu(II) ions. Only for the cyclohexylacetic acid the formation of further two, also mononuclear ML_3^- and ML_4^{2-} complexes was found. The values of pK_a of the studied acids and the values of the consecutive concentration stability constants obtained from the potentiometric and spectrophotometric measurements are given in Table 1. In both experimental methods the values of $\log\beta_1$ and $\log\beta_2$ were determined with an error not larger than ±0.02 and 0.03 respectively and 0.05 for $\log\beta_3$ and $\log\beta_4$.

Table 1. Stability constants of Co(II), Ni(II) and Cu(II) complexes with carboxylic acids (μ = 0.1 $NaClO_4$, T = 20°C).

Acid	pK_a	Metal ion (II)	ML^+ $\log\beta_1$		ML_2 $\log\beta_2$		ML_3^- $\log\beta_3$		ML_4^{2-} $\log\beta_4$	
			pot.	sp.	pot.	sp.	pot.	sp.	pot.	sp.
Methoxyacetic	3.25	Co	1.47	1.49	2.21	2.19	–	–	–	–
		Ni	1.59	1.61	2.44	2.41				
		Cu	2.23	2.22	3.72	3.74				
Phenylacetic	4.07	Co	1.20	1.22	1.77	1.80	–	–	–	–
		Ni	1.30	1.29	1.89	1.91				
		Cu	1.97	1.99	3.09	3.12				
Acetic [1]	4.40	Co	1.59	1.60	2.21	2.23	–	–	–	–
		Ni	1.71	1.71	2.49	2.48				
		Cu	2.41	2.42	3.71	3.72				
Cyclohexylacetic	4.46	Co	2.31	2.33	4.01	4.04	4.58	5.03	5.22	5.18
		Ni	2.39	2.41	4.13	4.10	5.10	5.07	5.37	5.42
		Cu	3.05	3.05	5.37	5.39	6.18	6.23	6.69	6.63

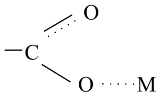
pot. – potentiometric method
sp. – spectrophotometric method

For the simplest studied acid, *i.e.* the acetic acid, which was a simple reference system in these studies, the number of registered complexes as well as the determined values of the stability constants were generally consistent with the data obtained by other authors [2,3], providing that we compared the concentration stability constants determined in the same conditions. The only exception is the Fronaeus paper of 1946 [18], who reported as many as four values of the stability constants for the Cu(II) acetate. It seems unlikely, if we take into account the Cu(II) coordination number on the one hand and the bidentate properties of the carboxylate ion on the other. It is known that in aqueous solutions this ion forms with the Cu(II) ions four-membered chelate complexes of low stability [19]



The methoxyacetic acid, the best dissociated among the studied acids (pK_a = 3.25), forms complexes that are more stable than complexes of the phenylacetic acid. Their stability is similar to those of the acetate complexes, despite the fact that the dissociation constant of the acetic acid is more than ten times smaller than the same constant of the methoxyacetic acid. There seems to be only one explanation of this significant increase in the methoxyacetic complexes' stability: the methoxyacetic acid binds the metal ions not only by the carboxylate ion, as in the case of the other acids, but also by the ether CH_3-O- group. A simple relationship between the pK_a value of the studied acids and the complex stability was found only for the acetic and phenylacetic acid complexes. The latter acid, as better dissociated than the acetic acid, forms clearly weaker complexes than the acetates. The complexogenic properties of the two acids with cyclic substituents, *i.e.* the phenyl- and cyclohexylacetic acids, are different than expected taking into account only their pK_a values.

The cyclohexylacetic acid forms complexes of about ten times higher stability than the phenylacetates,while the difference between their pK_a values is only 0.4 logK. This acid shows also much stronger complexogenic properties against all the studied bivalent metal ions than the acetic acid, although their pK_a values are practically identical. One can conclude that the only reason for this much stronger cyclohexylacetic acid – metal ion bond is a different way of the COO^- group coordination. Since only for the cyclohexylacetic acid as many as four complexes were registered and taking into account that these are mononuclear complexes, one can conclude that the carboxyl group in the cyclohexylacetic acid is monodentate [19,20]



and this type of the bond with metal ensures saturation of its coordination sphere. The question of unambiguous determination of the coordination type of the carboxylate ion and the metal in the solution is difficult and requires studies with appropriate spectroscopic methods. These studies have just been started.

Each of the acids studied forms with the Ni(II) ions slightly more stable complexes than with the Co(II) ions; this difference is not large and amounts to about 0.1 $\log\beta$. All the complexes with the Cu(II) ions of $3d^9$ electron structure are much more stable, which is obvious and results from the Jahn – Teller effect.

Finally, it can be added that, comparing the values of equilibrium constants obtained earlier for the Cu(II) – methoxy, – phenyl and – cyclohexylacetic acid system in the solutions of ionic strength equal to $\mu = 2$ [4] with the appropriate data obtained in this work for $\mu = 0.1$, the correction suggested in [1] for the recalculation of adequate concentration formation constants for the change at the ionic strength from 2 to 0.1, is fully confirmed. And thus, the protonation constants pK_a decrease by about 0.2, while stability constants $\log\beta_1$ and $\log\beta_2$ increase by about 0.1 $\log\beta$.

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