

## DISSERTATIONES

DCC-19 (Univ. Zagreb)

546.792.1.08:546.264

*Croat. Chem. Acta* 37 (1965)**Determination of the Composition and Stability of Complex Compounds of Thorium with Organic Dicarboxylic Acids by the Precipitation Method**

H. Bilinski-Matošić

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

The precipitation of thorium hydroxide in the pure system  $\text{Th}(\text{NO}_3)_4$  — KOH is compared with the precipitation in the same system to which organic dicarboxylic acids are added (phthalic, oxalic, maleic, and fumaric). All systems were prepared *in statu nascendi* and pH values were measured at equilibrium conditions. For the determination of different structures of the precipitates light and electron microscopes were used. The composition and characteristics of the formed precipitates were determined by chemical analysis, IR and NMR spectra. The composition of precipitates is:  $\text{Th}(\text{OH})_4$ , without water of crystallization;  $\text{Th}(\text{Phthalate})_2$ , without water of crystallization; Thorium hydroxy-phthalate, polymer with unknown formula.

The empirical formula, which gives the conditions for precipitation of thorium hydroxide in the presence of potassium phthalate was described. The number of OH ions per one thorium in soluble mixed complex of thorium with organic acids investigated was calculated.

Part of this thesis is published in *Croat. Chem. Acta* 35 (1963) 31

Examiners: Prof. B. Težak, Prof. D. Grdenić, and Prof. H. Iveković

Oral examination: November 25, 1964.

Degree conferred: May 22, 1965.

Thesis deposited at the University Library, Zagreb and Institute »Ruđer Bošković«, Zagreb.

(112 pages, 36 diagrams, 3 tables, 79 references, original in Croatian)

H. BILINSKI

DCC-19

546.792.1.08:546.264

1. Determination of the Composition and Stability of Complex Compounds of Thorium with Organic Dicarboxylic Acids by the Precipitation Method

I. Bilinski H.

II. Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

Complexes  
Fumarate  
Hydrolysis  
Maleate  
Oxalate  
Phthalate  
Solubility  
Thorium

DCC-20 (Univ. Zagreb)

546.33:546.792:546.56

*Croat. Chem. Acta* 37 (1965)**Square Wave Polarographic Behaviour of Uranium(VI) and Copper(II) in Aqueous Solutions of Acetylacetonone.**

Lj. Jević

*Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia*

Uranium (VI) forms complexes with acetylacetonone and the following ionic species, in accordance with free acetylacetonone concentration, are present in solution: free uranyl ( $\text{UO}_2^{++}$  ion, uranyl mono-acetylacetonato ( $\text{UO}_2\text{acac}^+$ ), and uranyl bis-acetylacetonato ( $\text{UO}_2\text{acac}_2^0$ ) complex ions. The three mentioned ionic species are polarographically reduced to one cumulative, s. w. polarographic peak.

The height of the peak is dependent on the concentration of free acetylacetonone as well as of the total acetylacetonone. When free uranyl ion is in excess in the solution, the s. w. peak height is constant. With increasing free acetylacetonone concentration the s. w. peak height decreases and passes through a minimum for the solution with highest uranyl mono-acetylacetonato concentration. Further increase of free acetylacetonone concentration is accompanied by increase of s. w. peak height which approaches the constant value when the uranyl bis-acetylacetonato complex ion is in excess in the solution.

On the basis of such results it was possible to calculate formal consecutive stability constants as:  $\log K_1 = 7.5$  and  $\log K_2 = 4.8$ .

Comparing the curves which represent the dependence of s. w. peak height on free acetylacetonone concentration with the curve which represents the theoretical distribution of the sum of the first and the third ionic species (if three ionic species are present in the solution) it was possible to calculate the over-all stability constant as:  $\log \beta_2 = 12.3$ .

It seems that adsorbed acetylacetonone, which forms an adsorption layer on the mercury surface, is specifically penetrable for the different mentioned ionic species.

On the basis of this assumption the influence of surface active agents on the s. w. polarographic reduction of uranyl acetylacetonone was investigated. Tritone-X-100, as a surface active agent, decreases specifically the s. w. peak height of each uranyl acetylacetonate species. From such specific depression the over-all stability constant of uranyl acetylacetonone complexes was calculated as:  $\log \beta_2 = 12.5$ .

In the case of copper acetylacetonato complexes, in s. w. polarographic conditions copper mono-acetylacetonato ( $\text{Cuacac}^+$ ) complex ion is reduced in a well defined peak. Due to that fact the curve which represents the dependence of s. w. peak height on free acetylacetonone concentration is identical with the theoretical distribution curve of second ionic species, if three ionic species are present in the solution.

On the basis of such results it was possible to calculate the formal and over-all stability constants as:  $\log K_1 = 8.8$ ,  $\log K_2 = 7.0$  and  $\log \beta_2 = 15.7$ .

Parts of this thesis were published and reported: *Croat. Chem. Acta* 35 (1963) 203; *ibid* 211; *Procs. 3rd Int. Congress of Polarography*, Southampton, July 1964, pp. 491-504.

Examiners: Prof. B. Težak, Prof. I. Filipović, and Dr. M. Branica.

Oral examination: July 13, 1964; Degree conferred: October 23, 1965.

Thesis deposited at the University Library, Zagreb and Institute »Ruđer Bošković«, Zagreb.

(112 pages, 30 figures, 170 references, original in Croatian).

LJ. JEVIĆ

DCC-20

546.33:546.792:546.56

1. Square Wave Polarographic Behavior of Uranium(VI) and Copper(II) in Aqueous Solution of Acetylacetone

I. Jeftić Lj.

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Complexes  
Copper(II)  
2,4-Pentanedione  
Polarography, s. w.  
Stability constants  
Surface active agents  
Uranium(VI)



DCC-21 (Univ. Zagreb)

547.291:542.952.6

*Croat. Chem. Acta* 37 (1965)**Fenomenology of the Precipitation Processes in Polymer Solutions.****Study of the Precipitation Processes of the System Formic Acid—Durethan—Nonsolvent by Means of Differential Precipitation Turbidimetry**

F. Flajšman

*Organsko Kemijska Industrija OKI, Zagreb, Croatia, Yugoslavia*

In order to obtain additional information on the factors influencing the possibility of molecular weight distribution analysis by means of turbidimetric precipitation titration, a modified method making possible the study of precipitation processes *in statu nascendi* has been applied to the various durethan fractions. Water, methanol, propanol, dioxane, and methylformate has been used as nonsolvents.

The method consists of the preparation of a series of independent precipitation systems by mixing each time 0.5 ml. of the polymer solution (0.2 g./100 ml.) with 9.5 ml. of one the solvent — nonsolvent mixtures covering the whole precipitation region. All stages of the precipitation process are followed by measuring the 135 degrees turbidity *vs.* time, by means of a visual Pulfrich photometer in three spectral region. Precipitation processes have been characterized by precipitation curves, time tyndallograms, and dispersion quotients. The following important requirements are fulfilled in this way:

- a) precipitation under constant concentration conditions
- b) the precipitate corresponding to the given amount of nonsolvent falls out as primary particles, and
- c) no influence of ageing on the correlation between turbidity and the amount of precipitate.

The primary and secondary precipitation processes can be registered separately. The nature of these processes is of predominant influence on the turbidimetric precipitation analysis, while the structure of the precipitate and the refractive index is of minor importance.

Precipitation behaviour with water as nonsolvent satisfies all requirements for molecular weight distribution analysis. Primary processes in alcohol media are very slow and induction periods are consequently observed, which are dependent on the solvent-nonsolvent ratio and molecular weight of the polymer. Dioxane and methylformate do not show precipitation selectivity on the molecular weight basis.

The precipitates consist of fibrils when water is used as nonsolvent, while typical spherulite aggregates arise with other nonsolvents. The tendency of the spherulites to aggregate increases with the decrease in the dielectric constant of nonsolvent.

*Examiners:* Prof. B. Težak, Prof. M. Mirnik, and Prof. R. Wolf.

*Oral Examination:* July 1, 1965; *Degree conferred:* October 23, 1965.

(118 pages, 23 figures, 5 electron micrographs, 97 references, original in Croatian)

F. FLAJŠMAN

DCC-21

547.291:542.952.6

1. Fenomenology of the Precipitation Processes in Polymer Solutions. Study of the Precipitation Processes of the System Formic Acid-Durethan-Nonsolvent by Means of Differential Precipitation Turbidimetry.

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Durethan  
Formic acid  
Nonsolvent  
Polymer solutions  
Precipitation processes, phenomenology  
Turbidimetry

MCC-12 (Univ. Zagreb)

547.963.32

*Master of Science Thesis**Croat. Chem. Acta 37 (1965)***Application of Labeled Compounds in a Study of the Metabolism of Ribonucleic Acid after X-irradiation***I. Pečevsky**Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia*

The metabolism of ribonucleic acid (RNA) was examined in exponentially growing cultures of *Escherichia coli B* irradiated with X-rays. Adenine-8-<sup>14</sup>C and adenine-3H were used to label the RNA synthesized in various periods before or after the irradiation. The radioactivity of the RNA fraction of irradiated and nonirradiated (control) culture was then compared.

A loss of approx. 25 per cent of radioactivity from the RNA fraction was observed in the cultures irradiated with 16,000 r, suggesting that part of the RNA had broken down in bacteria during the postirradiation growth. The effect was obtained with several doses of X-rays, and was proportional to the dose in the examined range. The RNA synthesized in the early periods of postirradiation growth was broken down at the same rate as the RNA synthesized before the irradiation.

*Examiners:* Prof. B. Težak, Dr. B. Miletić, Prof. V. Johanides, and Dr. M. Drakulić.

*Oral examination:* June 25, 1965.

Thesis deposited at the University Library, Zagreb and Institute »Ruder Bošković«, Zagreb.

(53 pages, 15 figures, 52 references, original in Croatian)

I. PEČEVSKY

MCC-12 (Univ. Zagreb)

547.963.32

1. Application of Labeled Compounds in a Study of the Metabolism of Ribonucleic Acid after X-irradiation

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Adenine-8-<sup>14</sup>C  
Adenine-3H  
Escherichia coli B  
Ribonucleic acid  
X-irradiation

MCC-13 (Univ. Zagreb)

547.544—8:541.124.546.11:546.11.02

Master of Science Thesis

*Croat. Chem. Acta* 37 (1965)**Secondary Isotope Effect in Solvolysis of Norbornyl Derivatives**

K. Humski

*Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia*

2-( $\Delta^3$ -Cyclopentenyl) ethyl-1,1- $d_2$  tosylate was prepared and converted to exo-norbornanol-6,6- $d_2$  by solvolysis in 80% aqueous acetic acid.

The proton magnetic resonance spectrum of this compound was recorded and the peak area integrated. The spectrum indicates 10–15% of 1,3-type deuterium migration.

Thus obtained exo-norbornanol was converted to the *p*-bromobenzenesulfonate and the rate constants for solvolysis in 100% acetic acid determined for the deuterated and undeuterated compound using an automatic recording pH-stat. A secondary isotope effect of ( $k_H/k_D$ ) 1.13 was observed.

The isotope effect and the observed hydrogen migration are discussed and possible explanations given.

On the basis of this work further investigations and experiments are planned.

Thesis was partly published: *Croat. Chem. Acta* 37 (1965) 3.

Examiners: Prof. B. Težak, Dr. D. E. Sunko, and Dr. I. Jambrešić

Oral examination: February 11, 1964 .

Thesis deposited at the University Library and Institute »Ruđer Bošković«, Zagreb.

(50 pages, 3 figures, 4 tables, 20 spectra, 27 references, original in Croatian.)

K. HUMSKI

MCC-13 (Univ. Zagreb)

1. Secondary Isotope Effect in Solvolysis of Norbornyl Derivatives

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547.544—8:541.124.546.11:546.11.02

Deuterium  
Isotope effect, secondary  
Hydrogen migration  
Norbornyl, derivatives  
Solvolysis

MCC-14 (Univ. Zagreb)  
Master of Science Thesis

542.65:546.799.1

Croat. Chem. Acta 37 (1965)

**Precipitation and Hydrolysis of Uranium (VI) Compounds in Aqueous Solutions**

B. Tomažič

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The conditions for the formation of precipitates in the systems: uranyl nitrate — potassium hydroxide — potassium nitrate have been studied. The compositions of the precipitates so formed were obtained by means of the polarographic method. The NMR-method was used for the characterisation of the hydration states of the dried precipitates. In the systems: uranyl nitrate — potassium hydroxide the ratio  $\text{UO}_2^{2+} : \text{OH}^-$  characteristic for the first appearance of precipitate, is dependent on the uranyl nitrate concentration. At a distinct ratio  $\text{UO}_2^{2+} : \text{OH}^-$  the content of progressive precipitation of uranium is decreased. On both sides of the precipitation minimum, the precipitates are visually different. Chemical analysis has shown that at higher  $\text{UO}_2^{2+} : \text{OH}^-$  ratios the heptauranate is formed, at lower ratios the composition corresponds to diuranate.

The system:  $1 \times 10^{-3}$  M uranyl nitrate and  $1.7 - 3.5 \times 10^{-3}$  M potassium hydroxide is optically clear, with no precipitation even after a prolonged period of time. The addition of potassium nitrate as »neutral electrolyte« causes the precipitation of potassium uranates. The ratio U/K decreases with increasing pH, it reaches the value 1 at pH 10 and keeps it above pH 10. The proposed action of the »neutral electrolyte« is incorporation of the cation into the formed precipitate, excluding the coagulation mechanism. NMR studies have shown the presence of hydroxyl groups and water of crystallization in the dried precipitates, the relative quantities being dependent on the experimental conditions.

Examiners: Prof. B. Težak, Prof. M. Mirnik, and Dr. M. Branica

Oral examination: December 13, 1963.

Thesis deposited at the University Library, Zagreb and Institute »Ruder Bošković«, Zagreb.

(72 pages, 17 figures, 9 tables, 62 references, original in Croatian)

B. TOMAŽIČ

MCC-14 (Univ. Zagreb)

542.65:546.799.1

1. Precipitation and Hydrolysis of Uranium (VI) Compounds in Aqueous Solutions

Precipitation  
Polarography  
Nuclear magnetic resonance  
Uranium

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MCC-15 (Univ. Zagreb)

542.61:546.72

*Master of Science Thesis**Croat. Chem. Acta 37 (1965)***The Study of the Third Phase Formed in the Extraction System:  
Ferric Chloride — Hydrochloric Acid—Water—Isopropyl Ether\****D. Maljković**Faculty of Technology, University of Zagreb, Sisak, Croatia, Yugoslavia*

Experimental investigations of heterogeneous systems: ferric chloride-water-isopropyl ether and ferric chloride-hydrochloric acid-water-isopropyl ether at 20°C were done.

On the basis of experimental results the equilibrium compositions of phases, tie lines in twophase region, isothermal curve and the type of the threecomponent system: ferric chloride-water-isopropyl ether are determined.

Qualitative diagrams of the volumenes of phases *vs.* quantity of one of the components in fourcomponent system: ferric chloride-hydrochloric acid-water-isopropyl ether in the conditions where the third phase is present, are given.

The equilibrium compositions of phases of the fourcomponent system in twophase and threephase region, for various initial concentrations of hydrochloric acid and ferric chloride are also determined. On the basis of these results orthogonal projections of points representing the compositions of phases in tetrahedral model are drawn.

Stability of isolated third phase during the period of six months is investigated.

Finally the results are discussed from the point of view of physico-chemical separation methods and compared with earlier published results by other authors.

*Examiners:* Prof. B. Težak, Dr. M. Branica, and Prof. C. Đorđević.

*Oral examination:* November 22, 1965

Thesis deposited at Institute »Ruder Bošković« and University Library, Zagreb.

(139 pages, 16 tables, 49 figures, 100 references, original in Croatian)

D. MALJKOVIĆ

\* Thesis was done in the Department of Physical Chemistry of the Institute »Ruder Bošković«.

MCC-15 (Univ. Zagreb)

542.61:546.72

1. The Study of the Third Phase Formed in the Extraction System: Ferric Chloride-Hydrochloric Acid - Water - Isopropyl Ether.

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Faculty of Technology, University of Zagreb, Sisak, Croatia, Yugoslavia

Equilibrium compositions  
Ferric chloride  
Isopropyl ether  
Liquid-liquid extraction  
Orthogonal projections of the points of threedimensional model  
Stability of third phase  
Third phase  
Three- and fourcomponent systems

MCC-16 (Univ. Zagreb)

542.8:546.79

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

**Preparative Continuous Electrophoretic Separation of Radionuclides and Components of Cyclotron Targets in Oxalic Media**

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An electrophoretic separation on model systems of magnesium [ $\text{Na}^{22}$ -Mg-Al] and rubidium [ $\text{Rb-Sr}^{90}$ -Y $^{90}$ ] cyclotron targets was studied. The optimal conditions for electrophoretic separations were obtained at  $10^{-2}$  M oxalic acid ( $\text{H}_2\text{OX}-\text{NH}_4\text{OH}$  . . . pH 5.5). Aluminium (yttrium) migrates to the anode, sodium (rubidium) to the cathode, while magnesium (strontium) does not show any considerable migration rate. The optimal conditions were applied for continuous electrophoretic technique a separation of carrier free  $\text{Na}^{22}$  and  $\text{Ba}^{133}$  on tracer level was performed from the irradiated magnesium and cesium cyclotron target respectively. The anodic dissolution of irradiated magnesium cyclotron target in oxalate medium was studied in view of shortening the time of the actual electrophoretic separations. Under the given experimental conditions it was possible to separate the complete cyclotron target in 10 to 12 hours.

This work was particularly presented on *The 10-th Meeting of the Chemists of P. R. Serbia*, Beograd, Yugoslavia, January 1963 and on the *Symposium on the Mechanism of Separation Processes in Radiochemistry*, Herceg Novi, Yugoslavia, October 1965.

Examiners: Prof. B. Težak, Dr. Z. Pučar, and Dr. M. Branica.

Oral examination: September 10, 1965.

Thesis deposited at the University Library and Institute »Ruđer Bošković«, Zagreb.

(88 pages, 28 figures, 62 references, original in Croatian)

V. JOVANOVIĆ

MCC-16 (Univ. Zagreb)

542.8:546.79

1. Preparative Continuous Electrophoretic Separation of Radionuclides and Components of Cyclotron Targets in Oxalic Media

Cyclotron targets  
Electrophoresys, continuous  
Radionuclides  
Separation, electrophoretic

I. Jovanović V.

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MCC-17 (Univ. Zagreb)

546.882—86:546.883—83

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

**Some Coordination Complexes of Niobium(V) and Tantalum(V)**

V. Katović

Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia

Complexes of the type  $\text{MX}_2\text{AcAc}(\text{OR})_2$ , where  $\text{M} = \text{Nb}(\text{V}), \text{Ta}(\text{V})$ ;  $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{AcAc} = \text{acetylacetonate}$ ;  $\text{R} = -\text{CH}_3, -\text{C}_2\text{H}_5$  have been prepared from the metal pentahalides and acetylacetonate in the parent alcoholic solutions. They are stable crystalline substances, but in solutions in alcohols interactions with solvent molecules occur, as evident from conductivity and molecular weight studies. Powder X-ray diffraction photographs have shown that the methoxy chloro and bromo derivatives of niobium and tantalum are isomorphous, the analogous ethoxy complexes forming another isomorphous group. Infra-red spectra have been analysed and a tentative assignment of some characteristic vibrational modes is given. Metal-ligand vibrational modes appear at frequencies close to those in other metal acetylacetonates and metal alkoxides.

Under similar experimental conditions, starting from  $\text{NbOCl}_3$  and acetylacetonate in methyl and ethyl alcohol solutions, complex derivatives of the same type,  $\text{NbCl}_2\text{AcAc}(\text{OR})_2$ , have been isolated. These results imply the unexpected solvolysis of the niobium-oxygen bond in alcohol solutions.

A compound of the formula  $(\text{NbOCl}_2\text{AcAc})_x$  has been isolated from the reaction of  $\text{NbOCl}_3$  with acetylacetonate. Infra-red spectrum of this oxo-dichloro-acetylacetonato niobium(V) reveals the presence of co-ordinated acetylacetonate and the vibrational modes of the niobium-oxygen double bond. Deuteration studies permitted the assignment of some bonds.

The thesis was reported in part at the 7<sup>th</sup> International Conference on Co-ordination Chemistry, Stockholm and Upsala, June 1962, and partly published: *J. Inorg. Nucl. Chem.*, 25 (1963) 1099; *Chem. and Ind.*, 1963, 411.

Examiners: Prof. C. Đorđević, Prof. D. Grdenić, and Prof. M. Mirnik.

Oral examination: October 17, 1963.

Thesis deposited at the University Library and Institute »Ruder Bošković«, Zagreb.

(56 pages, 4 figures, 5 references, original in Croatian)

V. KATOVIĆ

MCC-17 (Univ. Zagreb)

546.882—86:546.883—83

1. Some Coordination Complexes  
of Niobium(V) and Tantalum(V)

Complexes, coordination

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Niobium  
Tantalum

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MCC-18 (Univ. Zagreb)

547.449.03

Master of Science Thesis

Croat. Chem. Acta 37 (1965)

**Dipole Moments and Atomic Polarisation of Some Metallic Derivatives of 1,3-Diketones**

D. Sevdic

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Investigations of dipole moments of some metal acetylacetonates have shown, that in these molecules unexpectedly high values of the dipole moments have been calculated on basis of Everard *et al.* and Guggenheim method.

To get a better insight into this interesting phenomenon, measurements were carried out on a large number of co-ordination complexes of 1,3-diketones. Dipole moments of Be(II), Ni(II), Al(III), Fe(III), Th(IV), Zr(IV), Ce(IV), and V(IV) acetylacetonates were determined. For comparison with the literature data, measurements with Be(II), Al(III), Fe(III), Th(IV), and Zr(IV) acetylacetonates were repeated. Dipropionylmethane derivatives of Be(II), Cu(II) and Ni(II) were also examined, in order to see what is the influence of the chelate group change on the dipole moment value. Dipropionylmethane was used as ligand because its derivatives are better soluble in benzene than the metal acetylacetonates, and the measurements were therefore easier. Values of these dipole moments are discussed in comparison with the values received for metal acetylacetonates.

From experimental data obtained with acetylacetonates, the dipole moments have been calculated on basis of Everard *et al.* and Guggenheim method. By both methods the same dipole moment values were obtained. In consequence, dipole moments of dipropionylmethano metal complexes were derived only by Guggenheim method, which is more simple for calculations, as well as for the experimental work.

Examiners: Prof. D. Grdenić, Prof. C. Đorđević, and dr. M. Kesler.

Oral examination: April 1, 1964.

Thesis deposited at the University Library and Institute »Ruder Bošković«, Zagreb.

(80 pages, 62 references, original in Croatian)

D. SEVDIĆ

MCC-18 (Univ. Zagreb)

547.449.03

I. Dipole Moments and Atomic Polarisation of Some Metallic Derivatives of 1,3-Diketones

1,3-Diketones, derivates, metallic  
Dipole moments  
Polarisation, atomic

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MCC-19

541.486:543.876

*Master of Science Thesis**Croat. Chem. Acta* **37** (1965)

V. Simeon

**Chelating Properties of Some Natural Amino Acids***Laboratory of Analytical and Physical Chemistry, Institute for Medical Research, Yugoslav Academy of Sciences and Arts, Zagreb, Croatia, Yugoslavia*

Complex equilibria in solutions containing the ions of bivalent cadmium, copper, nickel, lead and zinc as well as optical isomers of alanine and phenylalanine, were studied by potentiometric titration method. The stability constants of complex species existing in such solutions were determined. The stabilities of complex species formed by investigated metals with enantiomeric forms of alanine and phenylalanine were found to be equal. A theoretical equation for the stability of complexes containing both *dextro* and *laevo* forms of the ligand was deduced. The *pK* values of alanine and phenylalanine were determined and correlated with the experimentally determined stability constants. Phenylalaninato complexes are by about 0.3 kcal/Mole more stable than would be expected on the ground of thermodynamic considerations. The fact could be explained by differences in solvation energies of alanine and phenylalanine molecules influencing the activity coefficients of the respective species.

*Examiners:* Prof. B. Težak, Prof. O. A. Weber, and Prof. C. Djordjević.

*Oral examination:* December 3, 1965.

Thesis deposited at the Central Chemical Library, Zagreb and Institute of Medical Research, Zagreb

(60 pages, 14 figures, 57 references, original in Croatian)

V. SIMEON

MCC-19

541.486:543.876

1. Chelating Properties of Some  
Natural Amino Acids

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Physical Chemistry, Institute for  
Medical Research, Yugoslav Aca-  
demy of Sciences and Arts, Za-  
greb, Croatia, Yugoslavia

Alanine  
Amino Acids  
Cadmium (II)  
Chelate Compounds  
Copper (II)  
Lead (II)  
Nickel (II)  
Optically active ligands  
Phenylalanine  
Zinc (II)

MCC-20

547.779:542.941.7.07

*Master of Science Thesis**Croat. Chem. Acta 37 (1965)*

**The Preparation and Properties of Tetrahydroindazolone  
Carboxylic Acids and Cyclohexylamino Acids  
as the Metals Sequestering Agents**

*V. Turjak-Zebić**Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia*

The dissociation constants and neutralization equivalents of tetrahydroindazolone carboxylic acids and cyclohexylamino acids in dioxane-water were determined by potentiometric micro-titrations. 2-Phenyl-4,5,6,7-tetrahydroindazol-3-one-5,5-dicarboxylic acid (FIDA) indicated chelating tendencies.

The complex-formation of the indazolone carboxylic acids with copper and alkaline earth metals was investigated potentiometrically.

The »up and down« method adopted for FIDA's testing shows low toxicity of FIDA and its possible use in physiological systems.

The quantitative separation of barium from strontium using FIDA as separating agent was described.

Thesis was partly published: *Croat. Chem. Acta 36 (1964) 221.*

*Examiners:* Prof. M. Proštenik, Prof. N. Allegretti, and Dr. V. Skarić

Thesis deposited at the Institute »Ruđer Bošković«, Zagreb.

*(66 pages, 16 figures, 3 tables, 53 references, original in Croatian)*

V. TURJAK-ZEBIĆ

MCC-20

547.779:542.941.7.07

1. The Preparation and Properties of Tetrahydroindazolone Carboxylic Acids and Cyclohexylamino Acids as the Metals Sequestering Agents

I. Turjak-Zebić V.

II. Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Cyclohexylamino acids  
Dissociation constants, determination of  
Metal sequestering agents  
Tetrahydroindazolone carboxylic acids

MCC-21

547.852.2

*Master of Science Thesis**Croat. Chem. Acta 37 (1965)***Microanalytical Determination of Sulphate in Conjugated Serotonin Metabolites***O. Hadžija**Institute »Ruder Bošković«, Zagreb, Croatia, Yugoslavia*

It was shown that Dodgson and Spencer microbenzidine method was not reliable in microdetermination of sulphate in *O*-sulphate conjugates, because the benzidine sulphate could not be freed completely from benzidine.

Antonopoulos modification of this method gave good results only when *O*-sulphate conjugates were hydrolyzed chemically. In enzymatic hydrolyzates obtained values of benzidine sulphate were constantly too low. It was found that the reason for the low values was a partial adsorption of sulphate on proteins.

A procedure was elaborated by which in enzymatic hydrolyzates of *O*-sulphate conjugates amounts of 100–200 µg. of sulphate could be determined within 1–2%. The proteins in hydrolyzate were precipitated with ethanol, centrifuged, the precipitate washed thoroughly twice with ethanol-water (1:1) and the sulphate was determined as benzidine sulphate colorimetrically in each fraction separately.

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O. HADŽIJA

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1. Microanalytical Determination  
of Sulphate in Conjugated Se-  
rotonin Metabolites

Conjugated Serotonin Metabolites  
Sulphate, microanalytical determi-  
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