# ACTA
# UNIVERSITATIS PALACKIANAE
# OLOMOUCENSIS

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## 2004

**ACTA**
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# CHEMICA 43

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ACTA UNIVERSITATIS PALACKIANAE OLOMUCENSIS
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# RESEARCH PROJECTS AT THE DEPARTMENT OF ANALYTICAL CHEMISTRY, FACULTY OF SCIENCE, PALACKY UNIVERSITY FROM 1960 to 1990

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**Abstract**

The work presents and gives order to works of employees of the Department. of Analytical Chemistry at the Faculty of Science, Palacky University in Olomouc in the period from 1960 to 1990.

**Key Words:** *Phenoxazine and phenothiazine dyes, phenoxazones, volumetric indicators, pesticides, degradation of polymers.*

In the period from 1960 to 1990 the Analytical Chemistry at the Faculty of Science of
the Palacky University was gradually included into several departments. Up to 1960 only one Department of Chemistry at the Faculty could be found situated at Křizkovsky Street. In September of that year the Department was divided. The Department of Inorganic Chemistry and Chemistry of Teaching Methods headed by professor Mečislav Kuraš remained at original place. After the Institute of Medical Chemistry had been moved from Lidicka street (at present Svoboda Street) the newly created Department of Analytical, Organic and Physical Chemistry was placed there. At the Head of the Department was the associate professor Eduard Ružička who in 1963 was appointed professor of Analytical and Organic Chemistry and in 1965 he obtained the scientific degree CSc., corresponding to Ph.D. degree. He stimulated the formation of the independent Department of Analytical Chemistry in 1969. As soon as in 1972 due to centralization the workplace of Analytical and Organic Chemistry was established and remained till 2001 when it was changed to the Department of Analytical Chemistry again.

Professor Růžička was at the head of the working team solving the state and contractual tasks in 1960 – 1985. Some scientific workers of other Universities marked the workplace of the Analytical Chemistry with a title „Indicator's school". Professor

Růžička was at the head of the Department till 1983 when he went into the retirement. In the presented projects he is listed as the first author of the solving team. The others of the solving team are presented in an alphabetical order.

Apart from the educational activity the employees of the Analytical Chemistry have been devoting to scientific–research activity[1,2] and to the cooperation with industrial plants at the north Moravia[3] since 1960. Unfortunately at that time the political activity together with the ideological one were preferred to education. It was the period of introducing the productive process into the education. Here some of the leadership of the Faculty of Science laid the great emphasis on that activity. In this period at the increased scientific-research activity an employee was examined if he does not ignore his political education of students. It was also the reason to refuse the employee advancement in career.

Since 1966 the solution of the state research projects have been performed according to five-years plans of the national economy.

In 1965 the workers of the Analytical Chemistry solved the sectional research project 0306 g titled **Study of Reactions and Complexes of Oxazones and Thiazones.** The research report includes 18 works. Their titles can be found in a bibliography of the publication activity of the research workers of the Faculty of Science, Palacky University[5].

Solving team: Ružička E, Adámek J., Juřina J., Kotouček M., Martinek M., Stránský Z., Stužka V.

Content: preparation of phenoxazine and phenothiazine dyes, their potentiometric determination, use as visual indicators in a volumetric analysis (neutralization and redox titration), determination of aliphatic acids as 2-alkylbenzimidazoles.

Substance and methods used: Thionoline, resazurine, resorufine, Meldol blue, muskarine, stannometry, askorbinometry, titanometry, bichromatometry.

In the cooperation with Lachema Brno seminar on syntheses, analytical properties of dyes in titration in aqueous and non-aqueous medium as neutralization and redox indicators, was realized in Olomouc.

On the basis of this cooperation two research reports of the project D-Ol-23-13/6-2 titled **Indicators Research** were presented. The first report with the title **Redox Indicators** has 67 pages and was defended in May, 30, 1966 in Brno.

The report was presented by: Ružička E., Stránský Z., Stužka V.

Content: preparation of resazurine ethers, resorufine, derivatives of phenoxaz-3-ones, titanometry, stannometry**.**

The second report **Acidobasic indicators,** p. 69, was defended in November, 4, 1966 in Brno.

The report was presented by: Ružička E., Stránský Z., Stužka V.

Content: preparation of 5-arylaminoderivatives of Meldola´s blue, muskarine and 7-aminophenoxaz-3-one. Spectrophotometric study of compounds, determination of their dissociation and relative constants of acidity. Connection between dissociation

constant and structure. Validation of Hammett equation. Application of compounds as indicators for titration in aqueous and non-aqueous media. Some compounds used: 9-dimethylaminobenzo/a/ phenoxazonium chloride (Meldola's blue), 2-hydroxy-9-dimethylaminobenzo/a/phenoxazonium chloride (muscarine), 9-dimethylaminobenzo/a/phenoxaz-5-one.

In the period from 1966 – 1970 the department solved the state research project I-4-4 titled: **Study of Analytical Properties of Heterocyclic Compounds and their Acidobasic and Oxidation – Reduction Indicators.** In this period four research reports of the mentioned state research project with following titles were defended:

1967 – **Mechanism of Syntheses and Properties of Phenoxazines Studied**

Ružička E., Adámek J., Haviger A., Juřina J., Kotouček M., Martinek M., Stránský Z., Stužka V.

Content**:** Study of the course of Kehrmann synthesis benzo/a/phenoxaz-5-ones using various methods (chemical, spectral and polarographic). Preparation of sulphoderivatives of Meldola´s blue. Behaviour of selected phenoxazine dyes in a strong alkaline medium. Reaction of nitrosonaphtols with phenols (resorcine, orcine) – some used compounds: benzo/a/phenoxaz-5-one, 7-hydroxyphenoxaz-3-one, 2-aminophenoxaz-3-one, benzo/a/phenoxaz-9-one, benzo/c/phenoxaz-9-one, 1,7,9-trihydroxyphenoxaz-3-ones (fluorein).

1968 – **Study of Physical and Analytical Properties of Some Phenoxazines**, p. 109

Ružička E., Čáp L., Dostál V., Haviger A., Stránský Z., Stužka V.

Content: Reaction of nitrosonaphtol with phenols and naphtols, study of arising benzo- and dibenzophenoxazones and their application as titanometric indicators and as indicators in a non-aqueous acetic acid. Determination of gold with methylene blue.

1969- **Preparation and Study of Physical and Analytical Properties of Some Hydroxyphenoxazones**

Ružička E**.,** Adámek J., Juřina J., Lasovský J.

Content: Physical and analytical study of reaction products of nitrosophenols with phenols. Explanation of reactivity of phenoxazine skeleton using quantum chemistry and MO-LCAO. The reaction of fluorein with cationts were studied and apparent stability constants were found. Specific reaction of $Cr^{2+}$ ions with resazurine, resorufine and benzo/a/- phenoxaz-9-one was studied. As a volumetric agent stannous chloride in glycerin-ethanolic medium was used for determination of some ions.

1970- **Physical Chemical and Analytical Study of Oxazines**

Ružička E., Adámek J., Bekárek V., Čáp L., Juřina J., Lasovský J., Kotouček M., Martinek M., Stránský Z., Stužka V.

Content: Other hydroxyphenoxazones were prepared and studied. Ultraviolet and infrared spectra of benzophenoxazones were presented and results were compared with their basicity. Protolytic properties of compounds in dependence on acidity of a solution were determined. Oscilopolarographic behaviour of benzoxazones was studied. Fluorein as a new complexometric indicator and its reactions with various ions was described. Application of phenoxazine dyes for photometric determination of some complexes with inorganic ions was described.

In the period from 1971 to 1975 the department solved the national research project IV- 3- 1 titled **Physical Chemical Study of Heterocyclic Compounds Regarding Their Constitution and Application in Chemistry.** In this period three partial research reports and the final research report were presented.

1971 – 1972 **Formation of Complexes and Application of New Agents and Indicators,** p. 171

Ružička E., Bekárek V., Čáp, L., Kotouček M., Lasovský J., Stránský Z., Stužka V.

Content: Spectrophotometric and amperometric study of fluorein complexes, 7-hydroxyphenoxaz-3-one, methylester of gallocyanine with various ions. Use of titanometry in a alkaline medium. Study of IR and H-NMR spectra of nitrophenoxazines and their application as neutralization indicators for the determination of some organic compounds. Polarographic behaviour of isorosindone derivatives. Protonation equlibria of derivatives of phenoxaz-3-one and gradual protonization of analytes.

1973 – 1974 **Some Heterocyclic Compounds Their Physical, Chemical and Analytical study,** p. 204

Ružička E., Adámek J., Bekárek V., Dostál V., Juřina J., Kandrnál J., Kotouček M., Lasovský J., Martinek M., Stránský Z., Stužka V., Šimek J.

Content: Preparation and study of other derivatives of phenoxaz-3-one, diaminoderivatives of Meldola's blue methylester, gallocyanine, isorosindone. Evaluation of ultraviolet and infrared spectra of hydroxybenzo/a/phenoxazines. Coulometric – titanometric determination of quinones. IR study of compounds with N-H bonds in various solvents.

1975 **Preparation and Equilibrium of Some Derivatives and Phenazine,** p. 178

Ružička E., Adámek J., Bekárek V., Dostál V., Jílek J., Juřina J., Kandrnál J., Kotouček M., Lasovský J., Stránský Z., Stužka V., Šimek J.

Content: Preparation and study of 5-hydroxybenzo/a/phenoxazine, dyes of alizarine green (sulphoderivatives of 6-hydroxydibenzo/a,j/phenoxaz-9-one) and methylester of gallocyanine. Determination of the composition of complexes with many cations and determination of stability constants. Application of other phenoxazine dyes for analytical determination using various methods.

1975 **Overall Report for 1971 – 1975.** Summary of results from the last period including, 5 chapters, p. 23

Ružička E., Adámek J., Bekárek V., Čáp L., Dostál V., Jílek J., Juřina J., Kandrnál J., Kotouček M., Lasovský J., Martinek M., Stránský Z., Stužka V., Šimek J.

In the period from 1976 to 1980 the national research project 4-2-1/4 with a title **Development of New Analytical Agents and Indicators.** In this period two partial research reports and the final research report were presented.

1976 – 1977 **Complex Equilibrium of Some Agents and Their Analytical Application,** p. 200

Ružička E., Adámek J., Bekárek V., Dostál V., Jílek J., Juřina J., Kotouček M., Lasovský J., Stránský Z., Stužka V., Šimek J.

Content: study of derivatives of alizarine green as complex agents**.** Study of properties and reactions of derivatives of gallocyanine. Study of unstable $Cr^{III}$ complexes

with some phenoxazines. Study of complexity and association of some N-H compounds by spectral methods.

1978 – 1979 **Analytical Use of Equilibrium and Reactions in Non-Aqueous Medium** Introduction and 13 contributions, p. 181.

Ružička E., Bekárek V., Dostál V., Jílek J., Stránský Z., Stužka V., Žujová S.

Content: Acidobasic equilibria and their influence on titration in non-aqueous media, influence of partial equilibria on the course of potentiometric titration curve. Homoconjugation of aromatic carboacids in acetonitril. Determination and power of acids in 4-methylpentane-2-one and determination of the bases power in 4-methylpentane-2-one. Nitrophenoxazines as neutralization indicators in acetone. Determination of sulfonamides and other compounds. Spectrophotometric study of acidobasic equilibria and polymeration of Nile blue A. Development of new identification methods in determination by gas chromatography.

1976 – 1980 **Final Report – Development of New Analytical Agents and Indicators,** p. 37

Ružička E., Adámek J., Bekárek V., Dostál V., Jílek J., Juřina J., Kotouček M., Lasovský J., Stránský Z., Stužka V., Šimek J., Žujová S.

Content: brief summary of results achieved in 1976 – 1979. Description of preparation of other derivatives of alizarine green, stability constant of complexes with cations and other analytical application of studied substance.

In the period from 1981 to 1985 (7th five-year plan) the radical change in the organization of the scientific research activity at Universities arised. The main project IV-3 with a title **Inorganic and Coordination Compounds** included the general task called IV-3-5 titled **Analytical Reactions and Methods** coordinated by Z. Holzbecher, professor of the Institute of Chemical Technology in Prague. The main project comprised three partial tasks: 01 titled **Study of Equilibrium, Mechanism, and Kinetics of Complex Formation Reactions** solved by Jaroslav Majer from Komensky University in Bratislava. This project included the research marked 101 of professor Jokl, the research task called 201 of associate professors Kuchar and Kandráč and the research task 301 of our professor Ružička. Our research project IV-3-5/01 301 was titled **Study of Reactions and Equilibria of Compounds with a Quinone Structure and Optimization of Methods of Microdetermination of Ions.** The partial project 02 including two tasks was solved by associate professor Vláčil and partial project 03 including six tasks was solved by associated professor Vrchlabský.

In the period 1981 – 1985 there was presented only the final report, p.21. It includes the introduction and presents the number of publications: 1981 – 7 reports, 1982 – 6 reports, 1983 -7 reports, 1984 – 7 reports and 1985 – 8 reports.

Solving team: Ružička E., Bekárek V., Dostál V., Kotouček M., Stránský Z., Stužka V., Šimek J.

The national project of the basic research IV-3-5/01 was presented on September, 26, 1985 at the Department of Analytical Chemistry, Faculty of Science, J.E. Purkyně University in Brno. All three parts of the project were rewiewed by the committee of oponents (Majer, Janák, Janča, Vavrouch, Šulcek, Novák). The oponent´s report was worked out by prof. J. Garaj from the Institute of Chemical Technology in

Bratislava and by prof. L. Sommer from the Faculty of Science, University of J.E. Purkyně in Brno.

In 1986 – 1990 (8th five-year plan) the research workers from the Department of Analytical Chemistry were involved in the solution of the primary main task of the national plan of the basic research titled **Input of Compounds of Chemical Nature into Ecosystem and Procedures of Their Transformations.** The project was coordinated by professor Eva Smolková. The Department of Analytical Chemistry solved the partial task titled **Analysis of a Small Amount of Pollutants in Liquid and Solid Phase.** The project comprised the study of biologically active compounds important in agriculture (pesticides) and in pharmacology (drugs). The project leader was the associate professor Zdeněk Stránský.

In 1974 – 1976 the department solved the problems of titanium white treatment on the basis of the lateral economic activity for the Moravian Chemical Plants in Přerov. Two research reports were defended in December 1974 and in September 1976:

**Treatment of the Surface of Titanium White,** p. 122

Ružička E., Stránský Z.

Content: the work presents treated samples of titanium white and describes the Metod of their evaluation.

**Study of the Surface of Titanium White and its Organic Treatment**

Ružička E., Stránský Z., Čáp L.

Content: 17 organic modificators were selected to be suitable for treatment of rutile white.These are polyethylenglycols, block copolymers of propylenoxide and its condensates, derivatives of fatty acids and aminosilanes.

In December 1975 the research project for MCHZ Přerov was defended called:

**Analysis of Premixes for Conformal Mass,** p. 88

Bekárek V., Šimek J.

Content: Identification and determination of some organic compounds in selected foreign premixes. It was found that these are premixes based on epoxide resins.

In 1976 – 1980 the partial research project of the Council of Mutual Economic Cooperation (RVHP) 116.10.5-2 was solved with a title **Differential Titrator for Potentiometric Titration** and in 1981 – 1987 another partial project 09.08.6.6 titled **Electroanalytical Module System** was presented. The national coordinator of the research was the associate professor Robert Kalvoda from the Institute of the Physical Chemistry and Electrochemistry of the Czech Academy of Science in Prague. The partial reports of the solved tasks were defended by the national coordinator at the international level in the coordination group for electrochemical instrumentation. The project was solved by J. Jílek.

The problems of the construction of electroanalytical device were included in the Czechoslovak Patent 7297-71, 19.10.1972 and in United States Patent 3,875,395, Apr.1, 1975 titled **Arrangement for Method of Obtaning a First, Second or Following Derivative of a Titration Curve (**J. Jílek, Palacky University in Olomouc). The patent was awarded by the International Valuation Committee at the 1er Salon

International des Inventions et des Techniques nouvelles, Geneve 18/26 Novembre 1972 and received the silver medal.

In 1978 – 1990 the department solved several research projects of the Main Fire Service Administration of the Ministry of the Interior of the Czech Republic in Prague and the Slovak Republic in Bratislava. The Department in Olomouc solved the partial tasks for the Department of the Technical and Fire Safety of the Industry at the Faculty of Mining Engineering in Ostrava. The responsible worker was at first associate professor Bohuslav Fait and later engineer Jiří Lošák. The responsible solver of the project was associate professor Petr Ševeček. The research of the workplace in Ostrava aimed to the analysis of the residua of heat degraded polymer plastics and study of these degraded products.

The main job content of the workplace in Olomouc was the interpretation of infrared spectra of degraded polymers and the elemental analysis of residua. Elemental analyses of the residua of degraded polymers using infrared spectra revealed the quality of a degraded product. This information is important for finding the seat of the fire from the criminal point of view. The results of the research were used in revealing the origin of burnt materials and the seat of the fire. All the research reports were presented in a written form and defended.

This researches resulted in a Catalogue of the fire properties of materials[6].

The research project V-124-070-04-04/04 titled:

**Study of Properties Changes of Selected Plastics and Non-metal Materials at Extreme Heat Stress.** The partial report defended in Ostrava, 1978, p. 106, 48 references.

Ševeček P., Neiser J., Zapletalová I., Stužka V.

Research project R-05-514-244-05

**Analysis of Solid Carbon Residua after Heat Degradation of Polymers.** Partial research report defended in Ostrava, October 1983, p. 110

Ševeček P., Stužka V., Neiser J.

Research project R-05514-224-05

**Analysis of Solid Carbon Residua after Heat Degradation of Polymers.** Final research report defended in Ostrava, September 1985, p. 82 and attachments.

Ševeček P., Stužka V., Neiser J., Dvořák P., Wodák P.

Research project R-05-514-125-03

**Analysis of Solid Products after Burning and its Application.** Final research report, p. 85, with literature and attachment defended in Ostrava, October 1990.

Ševeček P., Wodák P., Filipi B., Dvořák P., Stužka V., Neiser J.

In 1978 – 1990 problems of determination of trace concentrations of organic compounds and metals as impurities in sources of drinking water for Olomouc were studied on the basis of the lateral economic activity. The project was assigned by SmVAK 05 Olomouc.

The Department submitted 12 final reports titled: **Modification and Development of Methods for Determination of Organic Contamination in Drinking Water** (1978-1979); **Determination of Organic Contamination in Water** (1980 – 1984) and

**Determination of Organic Contamination in Drinking Water** (1985 – 1990), p. 862, including tables with results of analyses.

The reports were written by seniour lecturer Vladimír Dostál and the project was solved by Adámek J., Bekárek V., Čáp L., Havlínová A., Kotouček M., Peč P., Rieger S., Staňková O., Stránský Z., Stužka V., Šimková I., Tatarkovičová V., Žujová S.

In analysis of actual samples of untreated water from spring area Černovír, Chválkovice, Litovel, Příkazy a Senice contents of formaldehyde, acetone, di-ethylhexylphtalate, formic acid, acetic acid, lactic and phenoxyacetic acids, carbamates, triazines and pyrethroids, aliphatic, aromatic and halogen hydrocarbons, metals, were determined by modern instrumental methods of analytical chemistry.

Reports of research projects are committed to Archives of Palacky Univesity Olomouc.

## References


1. Ružička E., Březina F.: *Acta Univ. Palacki. Olomuc*., Fac. Rerum Natur. **53,** Chemica XVI, 211 (1977).
2. Stužka V.: *Acta Univ. Palacki. Olomuc*., Fac. Rerum Natur. **102**, Chemica XXX, 7 (1991).
3. Stránský Z., Ružička E., Březina F.: *Acta Univ. Palacki. Olomuc*., Fac. Rerum Natur. **73**, Chemica XXI, 121 (1982).
4. Urbášek P., Pulec J. and coll.: Chapters from the University history of education in Moravia from 1945 – 1990. Palacky University, Olomouc 2003.
5. Bibliography of publication activity of teachers at the Fakulty of Science, Palacky University in Olomouc from 1956 to 1965. Faculty of Science, Palacky University, Olomouc 1966.
   Bibliography of publication activity at the Faculty of Science, Palacky University in Olomouc from 1966 to 1975. Fakulty of Science, Palacky University, Olomouc 1977.
   Bibliography of publication activity at the Faculty of Science, Palacky University in Olomouc from 1976 to 1985. Fakulty of Science, Palacky University, Olomouc 1987.
   Bibliography of the Faculty of Science from 1986 to 1995. Palacky University, Olomouc 1995.
   Bibliography of the Faculty of Science from 1995 to 2000. Palacky University, Olomouc 2000.
6. Author's collective: Catalogue of fire properties of materials. MV SSR, HSPO, Bratislava 1984.


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# CHEMISTRY OF 1-ARYL-6-AZAURACIL-5-CARBONITRILES

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**Abstract**

Although 6-azauracil-5-carbonitriles and their 1-aryl derivatives represent quite large group of 6-azauracil derivatives, the review of their chemistry has not been published yet. This communication gives complete review of the mentioned compounds. The literature data are complete until 2004.

Chemistry of 1-aryl-6-azauracil-5-carbonitriles

1. Syntheses
   - 1.1. General synthetic procedures leading to 1-aryl-6-azauracils
     - 1.1.1. Cyclization methods
       - 1.1.1.1. Cyclization of N-[(arylhydrazono)-acyl]-carbamates
       - 1.1.1.2. Cyclization methods based on $C_2$-$N_3$ bond formation
       - 1.1.1.3. Cyclization methods based on $N_3$-$C_4$ bond formation
         - 1.1.1.3.1. Cyclization of 2-arylsemicarbazones of α-ketoacids
         - 1.1.1.3.2. Cyclization of arylsemicarbazones, resp. arylthiosemicarbazones of mesoxaldinitriles[72]
     - 1.1.2. Syntheses of 1-aryl-6-azauracils by arylation of 6-azauraciles
     - 1.1.3. Syntheses of 1-aryl-6-azauracils by rearrangement
     - 1.1.4. Syntheses of 1-aryl-6-azauracils by cleavage of some condensed [1,2,4]triazines
   - 1.2. Syntheses of 1-aryl-6-azauracil-5-carbonitriles
     - 1.2.1. Syntheses based on formation and following cyclization of ethyl arylhydrazonocyanacetylcarbamates
       - 1.2.1.1. Preparation and structure of ethyl arylhydrazonocyanoacetylcarbamates

**Introduction**

1-Aryl-6-azauracil-5-carbonitriles represent interesting derivatives of [1,2,4]triazines from point of view of the syntheses of many further derivatives and biologically active compounds.

Instead of correct name 2,3,4,5-tetrahydro[1,2,4]triazin-3,5-diones shorter trivial name 6-azauracil is used in this communication.

Denotation of compounds:

(A) Ethyl cyanoacetylcarbamate
(B) Ethyl arylhydrazonoacetylcarbamate
(Ca) 1-Aryl-6-azauracil-5-carbonitriles
(Cb) 1-Aryl –3-methyl-6-azauracil-5-carbonitriles
(Cd) 1-Aryl-6-azauracil-5-carboxamides
(Ce) 1-Aryl-6-azauracil-5-carboxylic acids

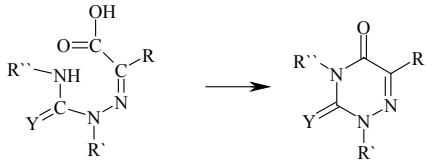
(D) Diethyl malonyl-bis-carbamate
(E) Diethyl arylhydrazono malonyl-bis-carbamate
(F) Ethyl N-(1-aryl-6-azauracil-5-carbonyl)-carbamate
(G) Cyanoacetamides
(H) Arylhydrazono cyanoacetamides
(I) N-Ethoxycarbonyl-N-arylhydrazonocyano-acetamides
(Ka) 1-Aryl-6-azauracils
(Kb) 1-Aryl-3-methyl-6-azauracils
(Kc) 1-Aryl-5-(2-hydroxy-1-naphtyl)-6-azauracils
(Kd) 1-Aryl-5-(o-mercaptophenyl)-6-azauracils
(L) 2-Arylsemicarbazones of glyoxylic acid
(M) Arylhydrazono malonodinitriles
(N) Isocyanates resp. Isothiocyanates
(O) 2-Arylsemicarbazones resp. 2-arylthiosemicarbazones of mesoxaldinitrile
(P) 1-Arl-6-azacytosines
(Q) 1-Aryl-3-subst.-6-azauracile-5-carbonitriles
(R) 6-Azauracile
(S) 1-(2-Subst.-4-nitrophenyl)-6-azauracile
(T) 2-Methylthio-6-azauraciles
(U) 1-(2,4-Dinitrophenyl)-2-methylthio-6-azauracils
(V) 1-(2,4-Dinitrophenyl)-6-azauracils
(X) 2-Benzylthio-3-benzyl-6-azauracil
(Y) 3-Aryloxy-4-benzyl-4,5-dihydro[1,2,4]triazin-5-one
(Z) 1-Aryl-3-benzyl-6-azauracils
(AB) 2-Aryl-2,3-dihydro[1]benzofuro[1,2,4]triazin-3-ones
(AC) Benzoderivatives of (AB)
(AD) 2-Aryl-2,3-dihydro[1]benzothieno[1,2,4]triazin-3-ones

The Arabic numeral designate the aryls of all compounds.

**1. Syntheses**

The cyclization of thiosemicarbazones resp. semicarbazones of α-ketoacids is the most usual synthesis of 6-azauracile ring.

*Scheme 1:*




Y = S, O

R, R`, R`` = –H, alkyl and aryl in various combinations.

A large number of variously substituted 6-azauracils (R = -H, alkyl, aryl; R´, R´´ = -H) have been synthesised in this way. Only a few N-alkyl, resp. N-aryl 6-azauracils was described in the literature so far. Complete information about these syntheses are summarized in reviews[1,2].

### 1.1. General synthetic procedures leading to 1-aryl-6-azauracils

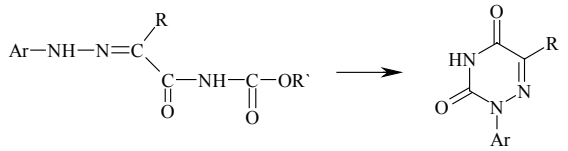
The above mentioned synthetic approach is not convenient for the synthesis of N-aryl-6-azauracils because of worse accessibility of starting compounds. In the following text there will be discussed synthetic methods based on cyclization or arylation of 6-azauracil cycle.

#### 1.1.1. Cyclization methods

The most advantageous methods are cyclizations based on $N_1$-$C_2$, resp. $C_2$ and $N_3$ bonds formation. The starting compounds are well accessible arylhydrazones. These hydrazones are obtained by coupling of aryldiazonium salts with compounds containing active methylene group.

##### 1.1.1.1. Cyclization of N-[(arylhydrazono)-acyl]-carbamates

*Scheme 2:*

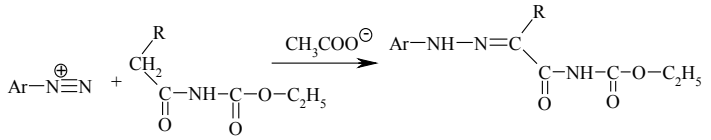


(*B*) R = –CN (*Ca*) R = –CN

(*E*) R = –CO–NH–$COOC_2H_5$ (*F*) R = –CO–NH–$COOC_2H_5$

Cyclization proceeds smoothly in basic medium or thermally[3-67].
The starting arylhydrazones (B) and (E), were prepared by coupling of aryldiazonium salts with ethyl cyanoacetylcarbamate (A) R = –CN[3-58] or with ethyl malonyl-bis-carbamate (D) R = –CO–NH–$COOC_2H_5$ [16, 61-67] in high yields.

*Scheme 3:*



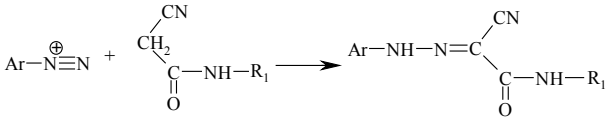
(*A*) R = –CN (*B*) R = –CN

(*D*) R = –CO–NH–$COOC_2H_5$ (*E*) R = –CO–NH–$COOC_2H_5$

### 1.1.1.2. Cyclization methods based on $C_2$ - $N_3$ bond formation

The starting arylhydrazono-kyanacetamides (H) were synthetised by coupling of aryldiazonium salts with cyanacetamide, resp. its N-methylderivative (Gb).

*Scheme 4:*



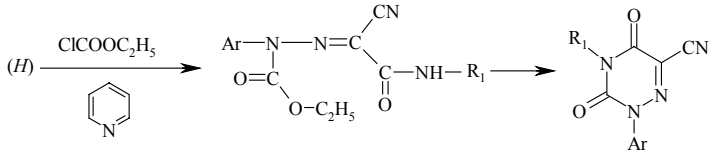
(*G*) (*H*)

a) $R_1 = –H$ b) $R_1 = –CH_3$

The cyclization of hydrazones (H) was than performed in 2 ways:

a) acylation with ethyl chloroformate and following thermal cyclization of N-ethoxy carbonylderivatives (*I*)[59, 60].

*Scheme 5:*

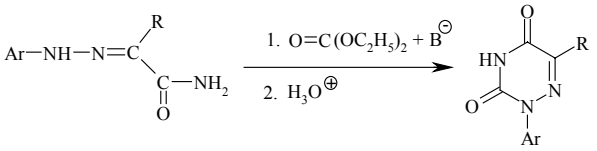


(*I*) (*C*)

a) $R_1 = –H$ b) $R_1 = –CH_3$

b) Cyclization by the action of diethylcarbamates in basic medium.
Here the N-ethoxycarbonylderivatives were cyclized without further isolation[68,70].

*Scheme 6:*



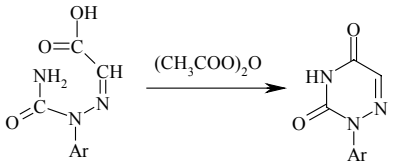
(*Ha*) R = –CN (*Ca*) R = –CN
(*Ja*) R = –H (*Ka*) R = –H

### 1.1.1.3. Cyclization based on $N_3 - C_4$ bond formation

#### 1.1.1.3.1. Cyclization of 2-arylsemicarbazones of $\alpha$-ketoacids

Only a few 2-arylsemicarbazones of glyoxylic acid were cyclized to azauracils (Ka) using the method mentioned in page 2.

*Scheme 7:*

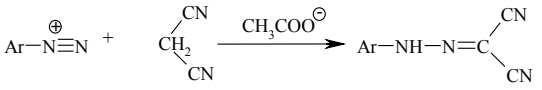



(*La*) (*Ka*)

#### 1.1.1.3.2. Cyclization of arylsemicarbazone, resp. arylthiosemicarbazones of mesoxaldinitriles[72]

The arylhydrazones of mesoxaldinitrile (*M*) are very well accessible by the coupling of aryldiazonium salts with malonodinitrile in high yields.

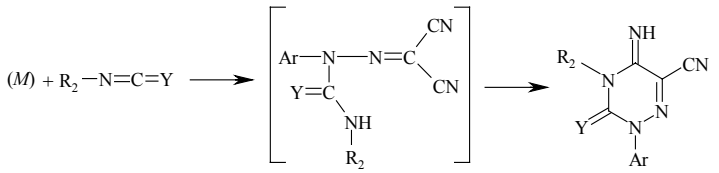
*Scheme 8:*




(*M*)

The acylation with isocyanates, resp. isothiocyanates leads to the semicarbazones (Oa, Ob)[72], resp. thiosemicarbazones (Oc, Od) that were without isolation cyclized to the corresponding 6-azacytosines (*Pa*, *Pb*), resp. 2-thio-6-azacytosines (Pc, Pd)[71].

*Scheme 9:*

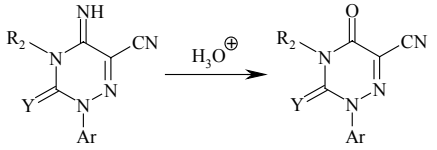



(*N*) (*O*) (*P*)

a) Y = O; $R_2 = -CH_3$ c) Y = S; $R_2 = -CH_3$

The hydrolysis under acidic conditions gave 3-substituted 1-aryl-6-azauracil-5-carbonitriles (Qa, Qb), resp. its 2-thioderivatives (Qc, Qd)[71].

*Scheme 10:*



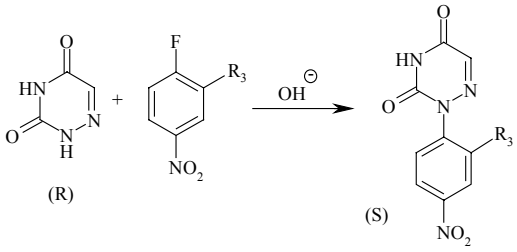
(*P*) (*Q*)

a) Y = O; $R_2$ = –$CH_3$ c) Y = S; $R_2$ = –$CH_3$

### 1.1.2. Syntheses of 1-aryl-6-azauracils by arylation of 6-azauracils

The arylation of 6-azauracil cycle was performed with the use of 4-nitrofluorobenzene and 2,4-dinitrofluorobenzene and and it proceeds to the 1-(4-nitrophenyl)-6-azauracil (Sa), resp. 1-(2,4-dinitrophenyl)-6-azauracil (Sb)[52, 54, 55, 57, 73].

*Scheme 11:*

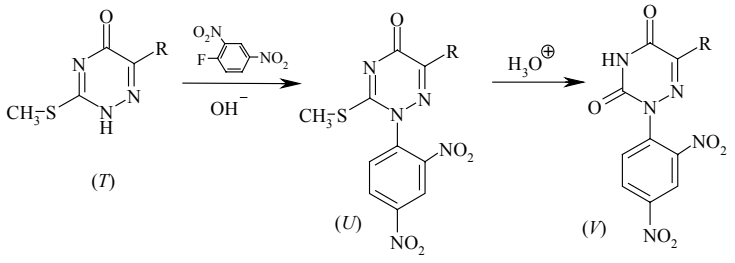


(R) (S)

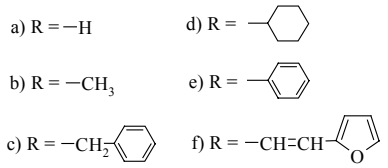
a) $R_3$ = –H b) $R_3$ = –$NO_2$

A number of 5-substituted 1-(2,4-dinitrophenyl)-6-azauraciles was also synthesized by the arylation of 5-substituted-2-methylthio-6-azauracils (T) and following acidic hydrolysis of 1-(2,4-dinitrophenyl)-derivatives (U)[74].

*Scheme 12:*



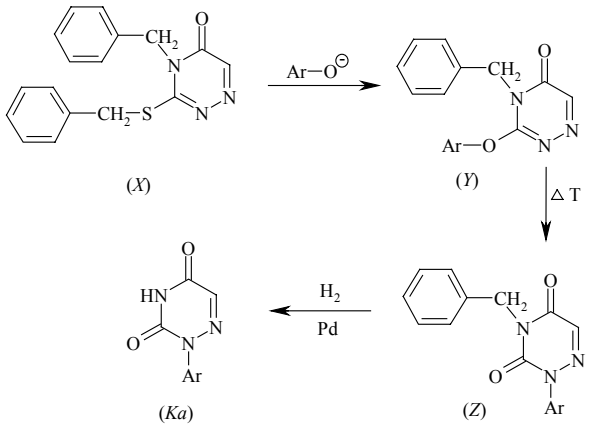
(*T*) (*U*) (*V*)




### 1.1.3. Syntheses of 1-aryl-6-azauraciles by rearrangement

There has been only 1 such method described till this time. The 3-aryloxy-4-benzyl-4,5-dihydro[1,2,4]triazin-5-ones (Y) are formed in the reaction of 3-benzylmercapto-4-benzyl-4,5-dihydro[1,2,4]triazin-5-one (X) with phenolate[75]. The 3-aryloxy-4-benzyl-4,5-dihydro[1,2,4]triazin-5-ones (Y) was not isolated and rearranges thermally to 1-aryl-benzyl-6-azauraciles (Z). Catalytic hydrogenolysis of (Z) gives 1-aryl-6-azauracils (Ka).

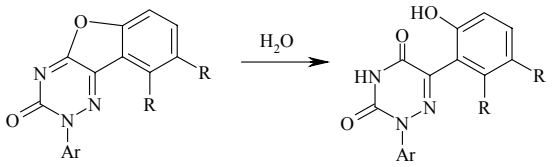
*Scheme 13:*




### 1.1.4. Syntheses of 1-aryl-6-azauraciles by cleavage of some condensed [1,2,4]triazines

The cleavage of furane, resp. thiophene ring condensed to the 1,2,4-triazine cycle seems to be interesting method of synthesis of 5-substituted 1-aryl-6-azauraciles. The hydrolysis proceeds very smoothly in the case of 2-aryl-2,3-dihydro-[1]benzofuro[1,2,4]triazin-3-one (AB) (R = - H)[76, 77] and its benzoderivatives (AC) (R+R = -CH=CH-CH=CH-)[78].

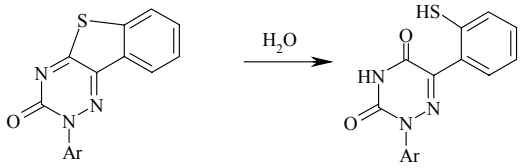
*Scheme 14:*




(*AB*) R = –H (*Kb*) R = –H
(*AC*) R+R = –CH=CH–CH=CH– (*Kc*) R+R = –CH=CH–CH=CH–

A series of 1-aryl-5-(2-hydroxyphenyl)-6-azauraciles (Kb), 5-(2-hydroxy-1-napthyl)-derivatives (Kc) as well as 1-aryl-5-(2-mercaptophenyl)-6-azauraciles (Kd) were prepared using this method[79].

*Scheme 15:*




(*AD*) (*Kd*)

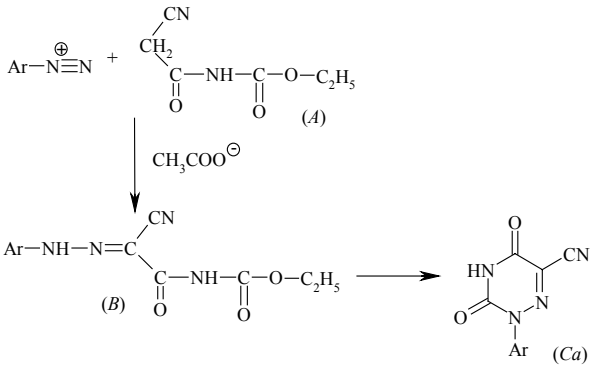
The starting compounds are obtained in high yields by coupling of aryldiazonium salts with ethyl N-(benzo[b]furan-2-yl)-carbamates, resp. benzo[b]thiophene derivatives[79].

### 1.2. Syntheses of 1-aryl-6-azauracil-5-carbonitriles (Ca)

As already mentioned there are two methods of cyclization leading to nitriles (C). In the first method the bond between atom 1 and atom 2 of 6-azauracile is formed, in the second method the bond between atom 2 and atom 3 of 6-azauracile cycle is formed.

### 1.2.1. Syntheses based on formation and following cyclization of ethyl arylhydrazonocyanacetylcarbamates

*Scheme 16:*

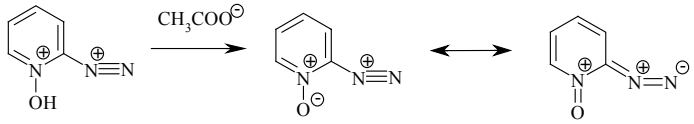


The mentioned synthetic route has been developed in Olomouc University already in 1963[3] and since this time it has been frequently used for the preparation of a great number of 1-aryl-6-azauracil-5-carbonitriles (Ca)[4-58], which have been used for preparation of other derivatives. The mentioned nitriles were not isolated in all cases[52-58]. A list of all isolated 1-aryl-6-azauracile-5-carbonitriles (Ca), in which the appropriate aryls are designated with Arabic numbers, is given at the end of this article.

#### 1.2.1.1. Preparation and structure of ethyl arylhydrazonocyanoacetylcarbamates

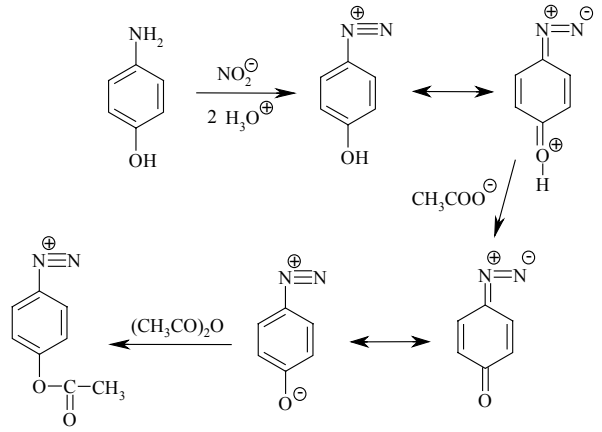
Because of double hyperconjugation of methylene group in ethyl cyanacetylcarbamates, causing their higher reactivity, their coupling with diazonium salts proceeds in high yields, even if less reactive diazonium salts are used. Suitable medium for the reaction is pyridine, in which carbamate (A) has a good solubility[3]. However more easier is procedure, in which solution of diazonium salt is added to aqueous solution of carbamate (A), buffered with sodium acetate. In this case it is necessary to dissolve the ethyl cyanoacetylcarbamate in hot water and rapidly cool it to an 0-5 °C. The coupling must be done before its precipitation from the solution. Without great problem it is also possible to make the coupling in suspension of carbamate (A).
In only one case, when hydrazone B122 was formed, it was necessary to make the coupling in strong acidic medium[34]. It is interesting, that in contrast to all known diazonium salts, N-oxidpyridin-2-diazonium salt is able to react also in acidic medium . In buffered medium coupling doesn't proceed, probably because of transfer of mentioned reactive protonized diazonium salt to nonreactive diazocompound.

*Scheme 17:*



Similar complications occur at compounds possessing group with +M effect, which are in buffered medium transformed to completely nonreactive forms. But in these cases coupling doesn´t proceed even in acidic medium. p-Aminophenol can serve as an example. During the diazotation it is transformed to a less reactive diazonium salt, which in buffered medium forms nonreactive diazooxide.

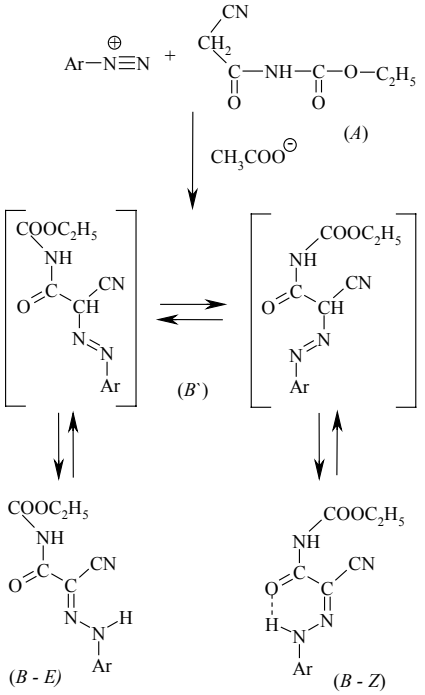
*Scheme 18:*



However this diazooxide is changed to the sufficiently reactive diazonium salt after acetylation, what means that hydrazone (Ba9) is possible to prepare in a good yield[30].

The question of geometric isomery of hydrazones (B)
Intermediates of azoderivates type (B´), formed during preparation of hydrazones, can undergo tautomerisation with the formation of E and/or Z isomer.

*Scheme 19:*



It is absolutely clear, that cyclization of hydrazones (B) to appropriate 1-aryl-6-azauracil-5-carbonitriles (Ca) can proceed at only Z isomers, whereas cyclization of E isomers is excluded because of steric reasons.

In accordance to the fact, that cyclization proceeds in mild condition, it was assumed that Z isomers, stabilized by intramolecular hydrogen bond, are formed during the coupling. Apparently this assumption was not in discrepancy to some spectral data[80,81].

But Lycka[82] established, with use of NMR study, the presence of mixture of isomers with predomination of E one in some similar hydrazones, formed after coupling of diazonium salts with other cyanoacetic acid derivatives. Because of these facts the structure of hydrazones (B) was corrected[83].

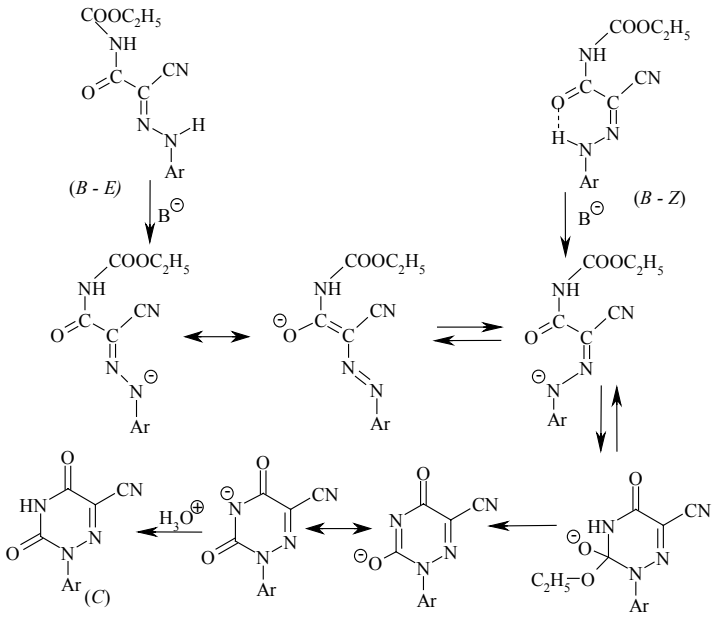
These facts resulted in theory, according to which easy isomerism of E isomer to Z one must proceed. It can be easily explained due to azohydrazono-tautomers, which causes free rotation of C-N bond (Scheme 19)

### 1.2.1.2. Cyclization of hydrazones (B)

All hydrazones (B) could be easily cyclized thermically or with use of an alkaline medium.

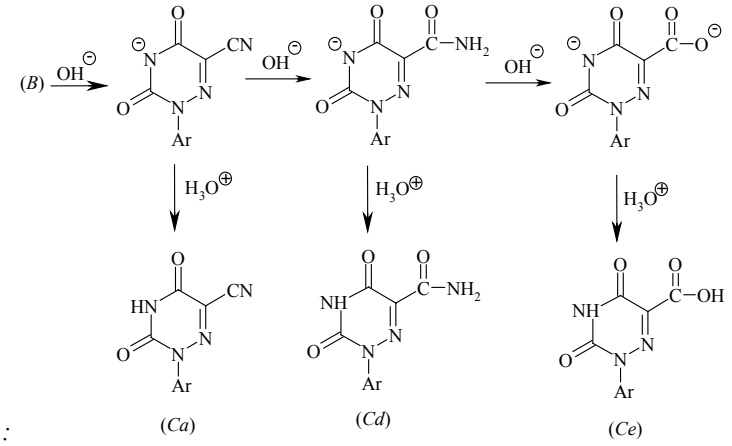
Alkaline cyclization affords salts of appropriate 1-aryl-6-azauracil-5-carbonitrile, acidification of which affords nitriles (C). Because of the easy isomerisation it doesn't depend on type of geometric isomer of hydrazone (B).

*Scheme 20:*



When alkaline solutions are used for cyclization, their concentration and reaction time are responsible for the composition of reaction mixture. It is obvious, that beside the main product also amides (Cd) or acids (Ce) can be formed after attack of nitrile group[3].

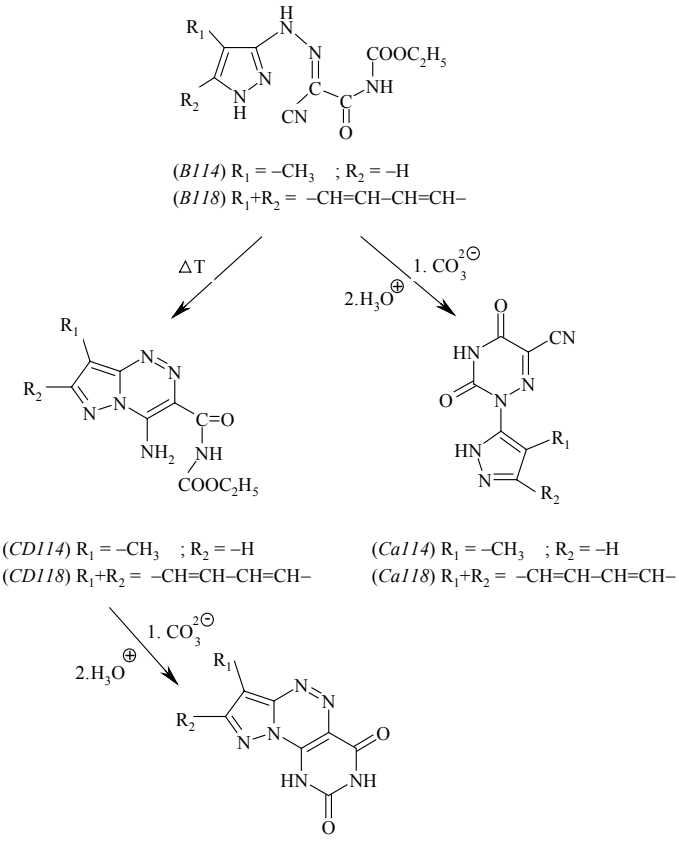
*Scheme 21:*



Therefore use of alkaline carbonates[5-58] or even bicarbonates[45,47] is more convenient. Thermal cyclization was made most frequently in xylene[3-58], in the case of less soluble hydrazones (B) decaline or nitrobenzene was used[29,34]. The easy cyclization of

hydrazones (B) proceeds by their heating to melting point[3,16] . Even use of nucleophilic solvents, like pyridine[10,40,41, 46, 50, 51, 59] or anisole[42, 43] is much more easier.
However thermal cyclization cannot be used in the case of hydrazones (B113) and (B117), because of different course of cyclization affording pyrazolo[5,1-c][1,2,4]triazine (CD114)[15] or [1,2,4]triazino[4,3-b]indazole (CD118)[19].
But alkaline cyclization in mild conditions affords 1-pyrazolyl-6-azauracils (Ca114) or indazolyl-6-azauracils (Ca118).

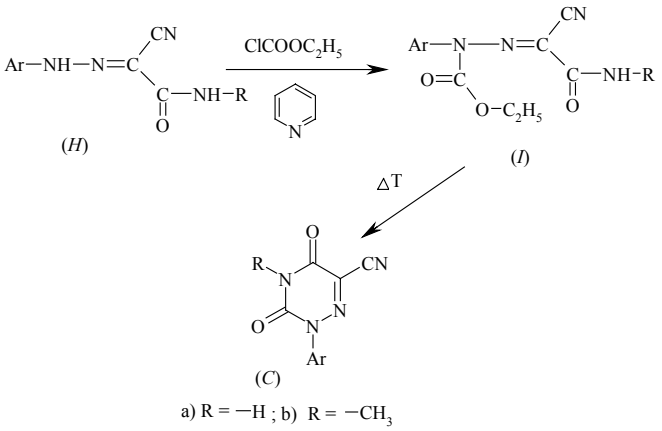
*Scheme 22:*




### 1.2.2. Syntheses based on preparation and cyclization of arylhydrazonocyanoacetamides

As it was mentioned in page 3, 1-aryl-6-azauracil-5-carbonitriles can also be formed by cyclization of arylhydrazonocyanacetamides (H) with use of ethyl chlorocarbonate. During this reaction acylation of hydrazone nitrogen atom proceeds first with formation of ethoxycarbonylderivative (I), which are consecutively cyclized to 1-aryl-6-azauracil-5-carbonitrile (C) at higher temperature.

*Scheme 23:*




Series of 3-unsubstituted 1-aryl-6-azauracil-5-carbonitriles (Ca)[59] and their 3-methylanalogues (Cb)[60] was prepared by this mode. Isolation of N-ethoxycarbonylderivatives (Ia) and their thermal cyclization was not used as often as reaction of hydrazone (H) with ethyl chlorocarbonate in pyridine solution. This reaction is made at low temperature with subsequent heating without isolation of intermediates (I)[59,60].

Although this procedure is easier, it is not as convenient as cyclization of ethyl arylhydrazonocyanacetylcarbamates (B), mentioned in previous chapter. It is probably caused not only by lower nucleophility of amidic group, but also by more difficult isomerization of E-isomers, unsuitable for cyclization, to isomers Z. List of all prepared 1-aryl-6-azauracil-5-carbonitrile (Ca) by the above mentioned methods and their 3-methylderivatives (Cb) is given in the end of this chapter.

## 2. The properties and conversion of 1-aryl-6-azauracil-5-carbonitriles

### 2.1. Physical and acidobasic properties of 1-aryl-6-azauracil-5-carbonitriles

If the molecules don't possess chromophoric group, they are colorless crystalline compounds, mostly with good solubility in organic solvents.

3-Unsubstituted derivatives (Ca) bearing acidic N-H group in their molecule, enable formation of hydrogen bonds, are noted for high melting points. Their acidity is higher then in case of uracil (pK = 9,43)[85] and because of influence of CN group even higher then in case of alone 6-azauracil (pK = 7,00)[84, 85] and it is comparable with acidity of carboxylic acids. By treatment of alkaline hydroxides, carbonates and bicarbonates they are transformed to alkaline salts, well soluble in water. Also ammonium, calcium, stroncium and barium salts posses good solubility.

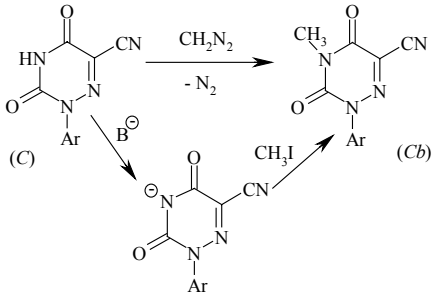
In the other hand 3-methylderivatives (Cb) are compounds with lower melting points, which lack acidic properties (if aryl doesn't contain acidic group).

Intensive bands in region of carbonyl vibrations are visible in IR spectra of all nitriles (C). However the most typical is the band of CN group at about 2240 $cm^{-1}$, which is shifted about 40 $cm^{-1}$ to higher values in comparison to hydrazones (B), e.g. reference[20].

### 2.2. Methylation of 1-aryl-6-azauracil-5-carbonitriles

Due to acidic character of NH group in nitriles (Ca), their methylation proceeds very easily to position 3 with use of diazomethane[60]. The same results are achieved after methylation of 1-aryl-6-azauracil-5-carbonitriles (Ca) with methyl iodide in alkaline medium[42].

*Scheme 24:*




### 2.3. Functional changes of nitrile group in 1-aryl-6-azauracil-5-carbonitriles

Nitrile group in compounds (C) is very reactive in sense of $A_N$ reactions.

#### 2.3.1. Adition of O-nucleophiles

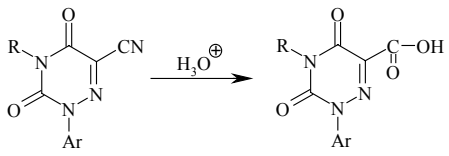
*a) Hydrolysis*

Alkaline hydrolysis occurs already during cyclization of hydrazones (B) with use of alkaline hydroxides[3] (see page 18). It is possible to get amides of 1-aryl-6-azauracil-5-carboxylic acids (Cd) and/or final acids in dependence on reaction conditions.

More general method for preparation of acids (Ce) is acidic hydrolysis commonly used by boiling of nitriles (Ca) with 20% hydrochloric acid[7-10, 13, 14, 16-18, 20-25, 27-35, 38, 40, 41, 43, 44, 49, 50, 86].

Acidic hydrolysis of 1-aryl-3-methyl-6-azauracil-5-carbonitriles (Cb) to acids (Cf) proceeds without problem.

*Scheme 25:*

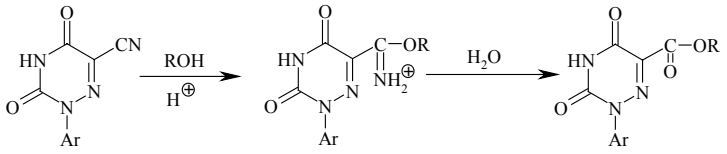



(*Ca*) R = –H (*Ce*) R = –H
(*Cb*) R = –$CH_3$ (*Cf*) R = –$CH_3$

*b) Addition of alcohols*

Nitriles (Ca) undergo addition of alcohols with the formation salts of iminoethere (Cg)[87, 88].

*Scheme 26:*



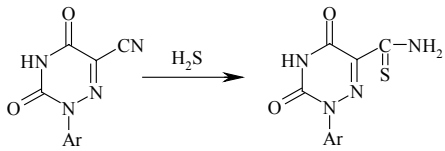

(*Ca*) (*Cg*) (*Ci*)

Iminoethers served for preparation of amides and amidines[87], but also esters (Ci). For preparation of esters (Ci) from nitriles (Ca) isolation of iminoethers is not necessary[88].

### 2.3.2. Addition of S-nucleophiles

Addition of sulphane is the only reaction of this type described up to now. This reaction affords appropriate thioamides of 1-aryl-6-azauracil-5-carboxylic acids (Cj)[4,7,9,11,34-36, 38-40].

*Scheme 27:*



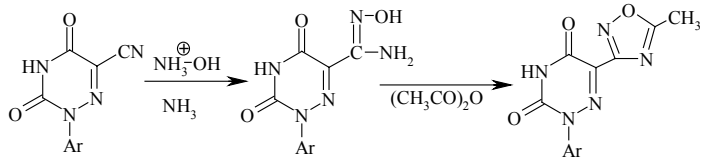

(*Ca*) (*Cj*)

### 2.3.3. Addition of N-nucleophiles

Only addition of hydroxylamine, affording amidoximes of 1-aryl-6-azauracil-5-carboxylic acids (Ck)[5, 7, 8, 17, 21, 23, 24, 30-35, 38, 40, 41, 44, 49, 87], is described in the literature.

Amidoximes have been frequently used for preparation of appropriate 1-aryl-5-(5-methyl[1,2,4]oxadiazol-5-yl)-6-azauracils (Cm)[5, 7, 8, 17, 21, 23, 24, 30-35, 38, 40, 41, 44, 49, 87].

*Scheme 28:*



(*Ca*) (*Ck*) (*Cm*)

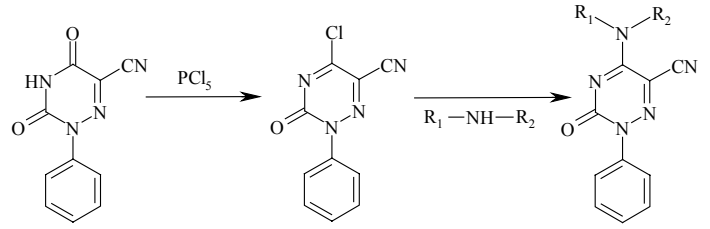
**2.4. Reactivity of carbonyl groups of 1-aryl-6-azauracil-5-carbonitriles**

Carbonyl groups of nitriles (Ca) differ in their reactivity towards nucleophiles. Carbonyl group in position 4 is more reactive. Up to now only a few reactions, based on nucleophilic addition in carbonyl group, have been made.

**2.4.1. Reaction of carbonyl group in position 4**

Only reaction of 1-phenyl-6-azauracil-5-carbonitrile (CaI) with $PCl_5$ is described[89].

*Scheme 29:*



(*Ca1*) (*Cn1*) (*Cp1*)

Heating of nitrile (CaI) with $PCl_5$ to 140-150 °C led to 2-phenyl-3-oxo-5-chloro-2,3-dihydro[1,2,4]triazine-6-carbonitrile (Cn1), which further served for synthesis of series of 1-phenyl-6-azacytosine-5-carbonitrile (Cp1)[89].

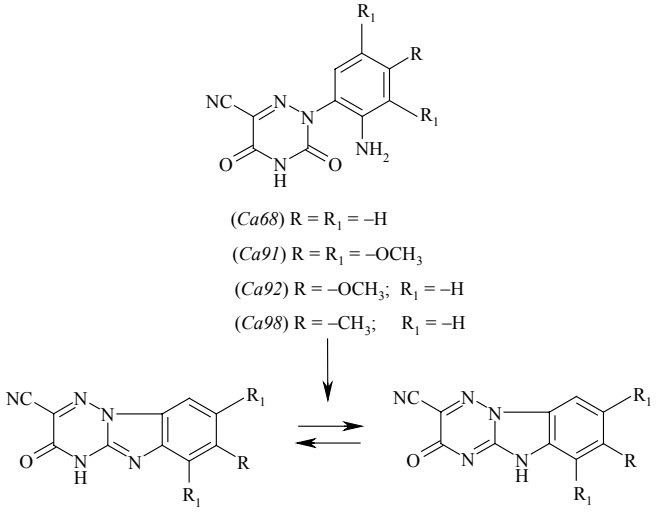
**2.4.2. Cyclocondensation reactions of carbonyl group in position 2 of compounds (C)**

Cyclocondenzation, leading to formation of condensed heterocycles, proceeds very easily, although carbonyl group in position 2 is less reactive.

*a) Cyclocondenzation of 1-(2-aminophenyl)-6-azauracil and its derivatives with formation of benzimidazole ring*

Heating to melting point, boiling in acetic acid[20,42] or boiling in anisole[42] carries out the reaction and affords appropriate derivatives of [1,2,4]triazino[2.3-a]benzimidazole.

*Scheme 30:*



(*Ca68*) R = $R_1$ = –H

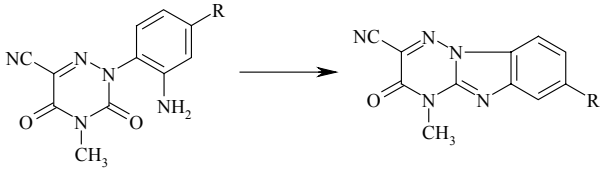
(*Ca91*) R = $R_1$ = –$OCH_3$

(*Ca92*) R = –$OCH_3$; $R_1$ = –H

(*Ca98*) R = –$CH_3$; $R_1$ = –H

Cyclocondenzation also proceeds at analogous 3-methylderivatives (Cb)[42].

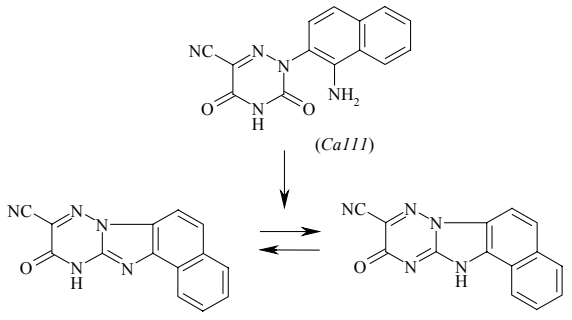
*Scheme 31:*



(*Cb68*) R = –H
(*Cb92*) R = –$OCH_3$
(*Cb98*) R = –$CH_3$

The cyclocondenzation of mentioned type was successfully used for synthesis of tetracyclic condensed compounds[49].

*Scheme 32:*

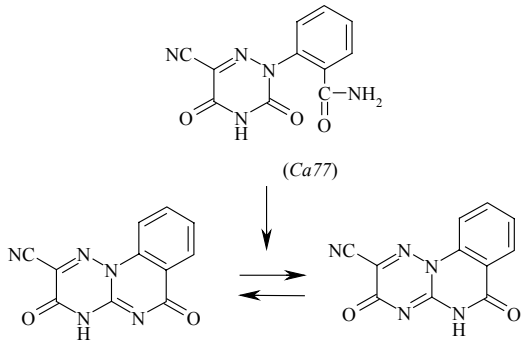


(*Ca111*)

*b) Cyclocondenzation with formation of quinazoline cycle*

Thermal cyclization of o-carbamoylphenylderivative (Ca77) affording 3,6-dioxo-3,4-dihydro-6H[1,2,4]triazino[2,3-a]quinazoline-2-carbonitrile or its 5,6-dihydro-3H-tautomer[16] belongs to this type of reaction.

*Scheme 33:*



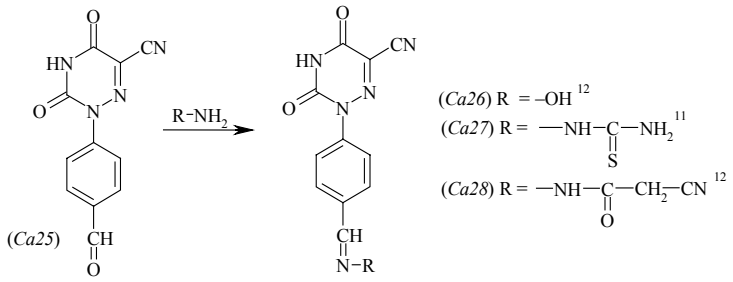

## 2.5. Reactions proceeding at aryl substituent

### 2.5.1. Functional transformation of groups bonded to aryl

Up to now only some functional transformations of groups bonded to phenyl ring have been described.

*a) aldehydic group*

*Scheme 34:*

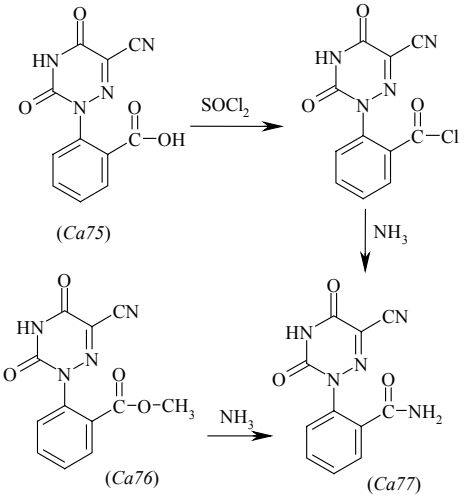



Mentioned synthetic route was used for easy preparation of oxime (Ca26), thiosemicarbazone (Ca27) and cyanoacetylhydrazone (Ca28)

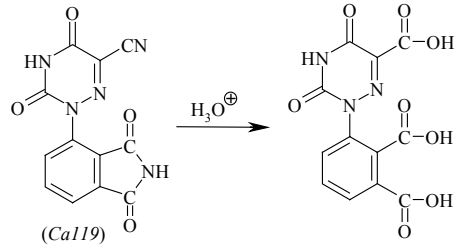
*b) carboxylic group and its functional transformation*

The formation of chloride and amide (Ca77) from acid (Ca75)[76] or hydrolysis of phtalimide derivative[18] belongs to this type of reaction.

*Scheme 35:*



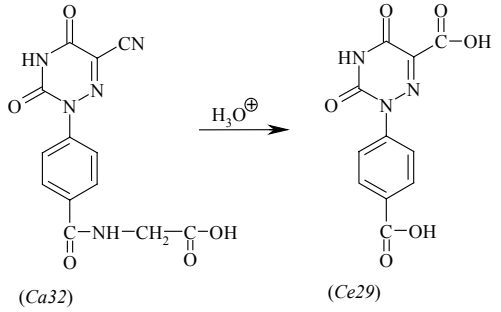

*Scheme 36:*




During this reaction hydrolysis of nitrile group in position 5 proceeds as well.

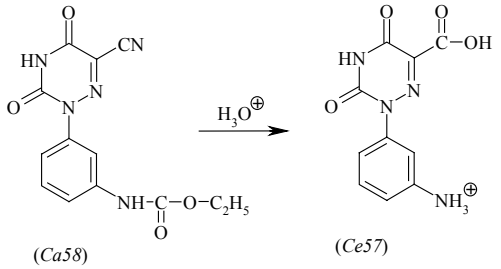
Similar course of reaction was observed during hydrolysis 4-(5-cyano-6-azauracil-1-yl)-hippuric acid (Ca32)[39].

*Scheme 37:*



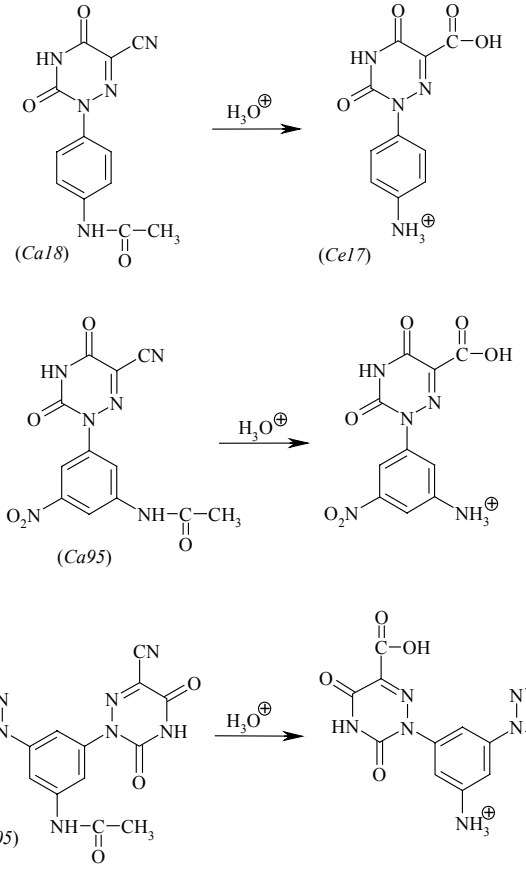
Nitrile group undergoes total hydrolysis also during splitting of acyl in acylaminoderivatives[40].

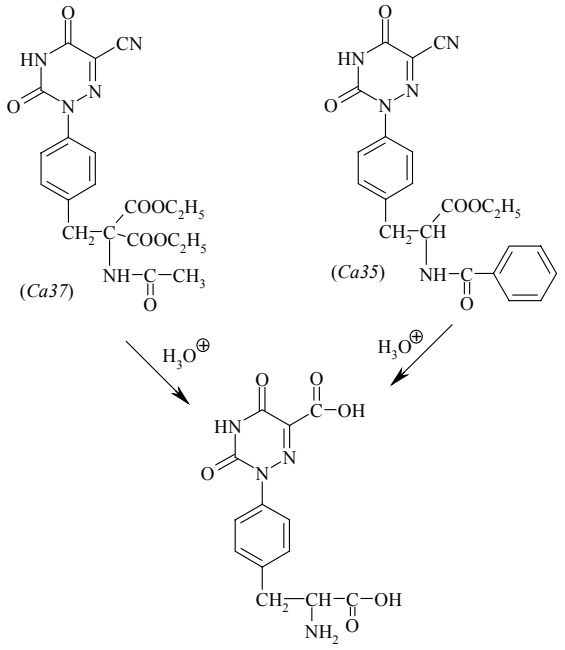
*Scheme 38:*




The similar behavior possesses hydrolytic splitting of acetyl[50].

*Scheme 39:*





During the last mentioned reaction the hydrolysis of all other functional groups proceeds as well and in the case of derivative (Ca37) it is accompanied also with decarboxylation[22].

Acidic hydrolysis led also to splitting of phtalyle[20].

The hydrolysis of phenolesters is easy as well[30].

Total hydrolysis of acylated N-amino group at nitriles (Ca36) and (Ca41) led to appropriate α-ketoacid[27].

### 2.5.2. Reduction of groups bonded to aryl

Very often transformations are reduction of nitroarylderivatives to appropriate aminocompounds.

The well-tried mode was reduction with $Fe(OH)_2$[20,37], which was obtained from ferrous sulphate after addition of aqueous ammonia or better $Ba(OH)_2$.

In the last case the solution is free of inorganic salts, which can complicate the isolation of product in some cases.

This route was used for preparation of m-isomer (Ca57)[37] , substituted derivatives (Ca91)[96], (Ca92)[42], (Ca98)[42], (Ca111)[49] , N-methylderivatives (Cb92)[42] and (Cb98)[42] as well.

Reduction with $SnCl_2$ in ethanolic solution was conveniently used for preparation of 4-aminophenylderivative (Ca17)[37].

Other type of reduction of nitro group like reduction with iron or $SnCl_2$ in acidic medium leads to parallel hydrolysis of nitrile group.

The similar course of reaction was observed during reduction with ammonium sulphide, when parallel addition of sulphane to nitrile group proceeds[40].

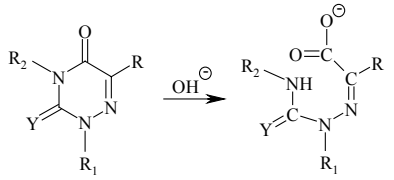
Also the reduction of arsenic group was made in one case[21].

**2.6. The cleavage of 6-azauracil ring.**

6-Azauracil ring is very stable against hydrolytic cleavage if it is not substituted at atom N in position 3.

But 3-alkyl-6-azauracils treated in alkaline medium undergo hydrolytic cleavage of cycle between atoms 3 and 4 with formation of appropriate α-ketoacid semicarbazones or thiosemicarbazones respectively[84, 90-92].

*Scheme 40:*

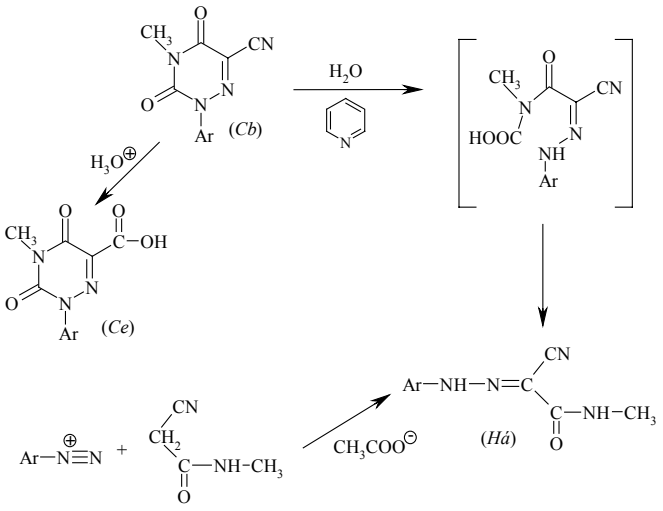



Y = –O, –S

3-Ribofuranosylderivative[93] or 3-aminoderivative[94] undergo the same mode of the ring opening.

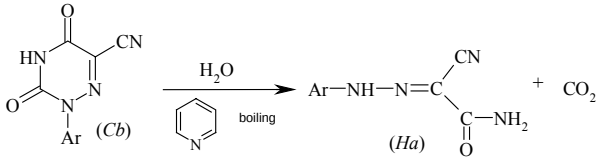
Absolute different behavior is typical for 1-aryl-3-methyl-6-azauracil-5-carbonitriles (Cb). While the acidic medium causes only hydrolysis of nitrile group with leaving the 6-azauracile ring unchanged, boiling in aqueous pyridine causes the cleavage between atoms 1 and 2 with rise of acylated carbamic acid. This acid immediately decarboxylates, so the product of the reaction is corresponding arylhydrazonocyanacetamide (Ha)[60]. For structure comparison hydrazones (Ha) were prepared also by coupling reaction[60].

*Scheme 41:*



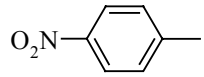
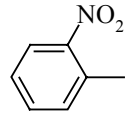
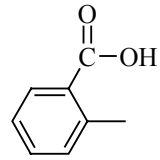
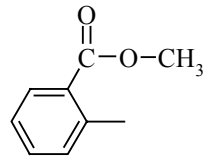
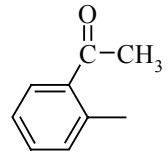
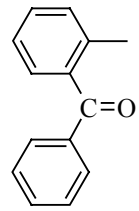
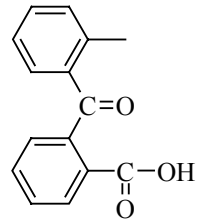
It was found out, that in case of 1-aryl-6-azauracile-5-carbonitriles unsubstituted in position 3 (Ca) boiling in aqueous pyridine causes the hydrolytic cleavage of cycle of the above mention type. But only in case, when aryl contains a group with –M effect, like at compounds (Ca19), (Ca72), (Ca75), (Ca76), (Ca79), (Ca80), (Ca81) and (Ca113).

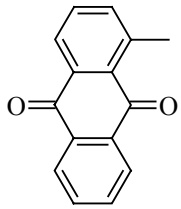
*Scheme 42:*



The summary of arylhydrozonocyanacetamides prepared by above metioned method is in table 1.

Tab. 1: Arylhydrazonocyanoacetamides (*Ha*)

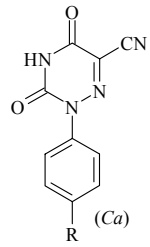
| Number of aryl | Ar | Reference |
|---|---|---|
| 19 |  | 10 |
| 72 |  | 20 |
| 75 |  | 16 |
| 76 |  | 16 |
| 79 |  | 29 |
| 80 |  | 29 |
| 81 |  | 29 |

| The continuation of Table 1 | | |
|---|---|---|
| 113 |  | 29 |

## 3. Summary of described 1-aryl-6-azauracil-5-carbonitriles (*Ca*, *Cb*)

### 3.1. Phenyl and substituted phenylderivatives

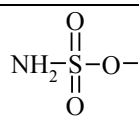
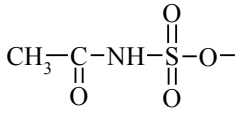
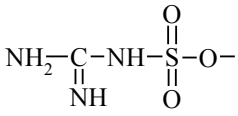
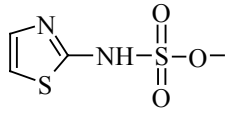
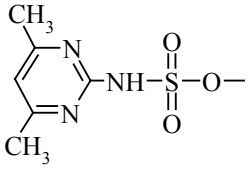
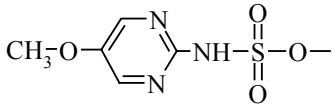
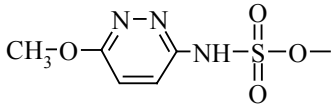
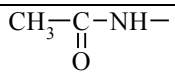
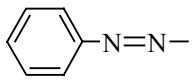
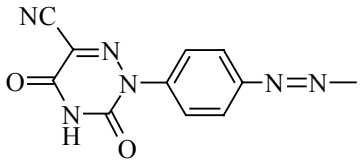
#### 3.1.1. *p*-Substituted phenylderivatives



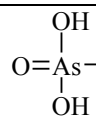
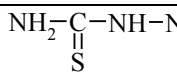
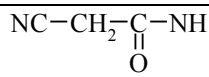
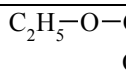
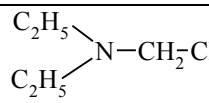
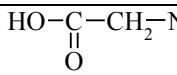
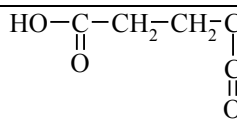
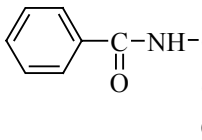
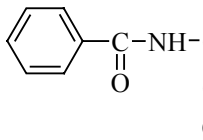
(*Ca*)

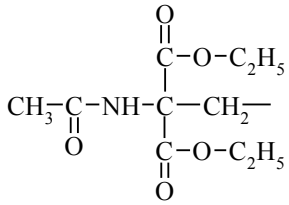
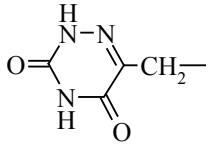
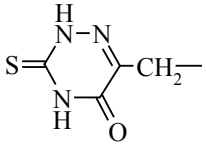
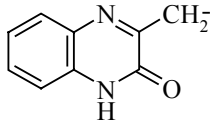
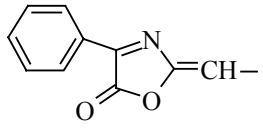
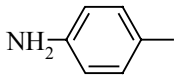
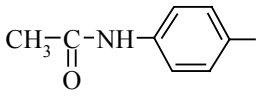
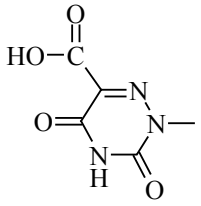
Tab. 2: *p*-Substituted phenylderivatives

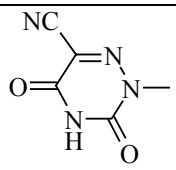
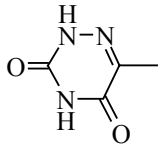
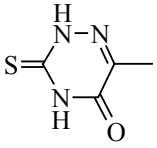
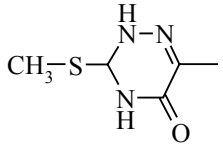
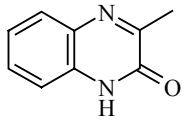
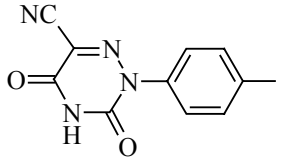
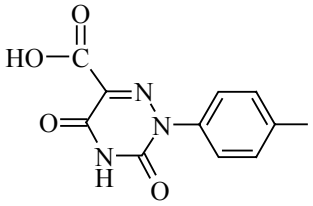
| Compound | R | Reference |
|---|---|---|
| *Ca1* | H- | 3, 4, 5, 59 |
| *Ca2* | F- | 12 |
| *Ca3* | Cl- | 4, 5, 59 |
| *Ca4* | Br- | 3, 4, 5, 59 |
| *Ca5* | I- | 4, 5, 59 |
| *Ca6* | HO- | 30 |
| *Ca7* | $CH_3$—O— | 4, 5, 59 |
| *Ca8* | $C_2H_5$—O— | 4, 5, 59 |
| *Ca9* | $CH_3$—C(=O)—O— | 30 |

| The continuation of Table 2 | | |
|---|---|---|
| *Ca10* |  | 9 |
| *Ca11* |  | 26 |
| *Ca12* |  | 26 |
| *Ca13* |  | 26 |
| *Ca14* |  | 26 |
| *Ca15* |  | 26 |
| *Ca16* |  | 26 |
| *Ca17* |  | 37 |
| *Ca18* |  | 10 |
| *Ca19* |  | 10 |
| *Ca20* |  | 33 |
| *Ca21* |  | 33 |

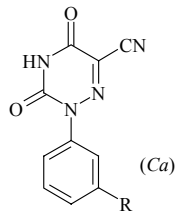
The continuation of Table 2

| | | |
|---|---|---|
| *Ca22* |  | 21 |
| *Ca23* |  | 21 |
| *Ca24* |  | 3, 4, 5, 59 |
| *Ca25* |  | 11 |
| *Ca26* |  | 12 |
| *Ca27* |  | 11 |
| *Ca28* |  | 12 |
| *Ca29* |  | 9 |
| *Ca30* |  | 9 |
| *Ca31* |  | 12 |
| *Ca32* |  | 39 |
| *Ca33* |  | 39 |
| *Ca34* |  | 9 |
| *Ca35* |  | 22 |
| *Ca36* |  | 27 |

| The continuation of Table 2 | | |
|---|---|---|
| *Ca37* |  | 22 |
| *Ca38* |  | 28 |
| *Ca39* |  | 28 |
| *Ca40* |  | 48 |
| *Ca41* |  | 27 |
| *Ca42* |  | 31 |
| *Ca43* |  | 31 |
| *Ca44* |  | 14 |

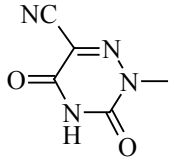
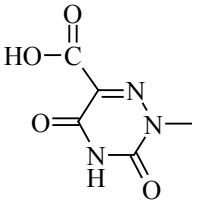
| The continuation of Table 2 | | |
|---|---|---|
| *Ca45* |  | 24, 37 |
| *Ca46* |  | 23 |
| *Ca47* |  | 23 |
| *Ca48* |  | 23 |
| *Ca49* |  | 48 |
| *Ca50* |  | 13, 31 |
| *Ca51* |  | 31 |

### 3.1.2. *m*-Substituted phenylderivatives

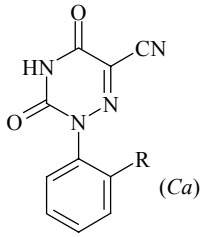



(*Ca*)

Tab. 3: *m*-Substituted phenylderivatives

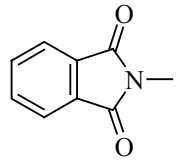
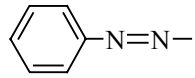
| Compound | R | Reference |
|---|---|---|
| *Ca52* | F- | 12 |
| *Ca53* | Cl- | 12 |
| *Ca54* | Br- | 12 |
| *Ca55* | I- | 12 |
| *Ca56* | $CH_3-O-$ | 12 |
| *Ca57* | $NH_2-$ | 37 |
| *Ca58* | $C_2H_5-O-\overset{\overset{O}{\|}}{C}-NH-$ | 40 |
| *Ca59* | $O_2N-$ | 6, 37 |
| *Ca60* | $CH_3-$ | 12 |
| *Ca61* | $HO-\overset{\overset{O}{\|}}{C}-$ | 12 |
| *Ca62* |  | 37, 40 |
| *Ca63* |  | 40 |

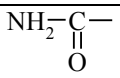
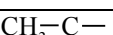
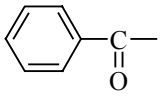
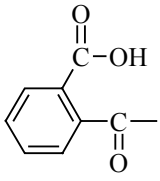
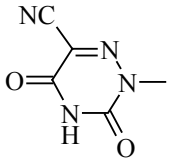
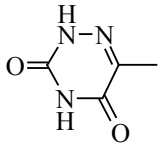
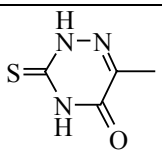
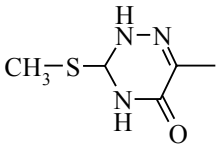
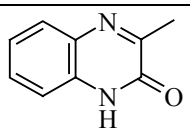
### 3.1.3. *o*-Substituted phenylderivatives

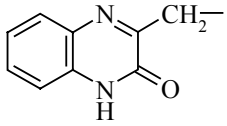


(*Ca*)

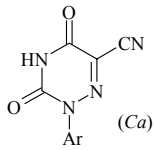
Tab. 4: *o*-Substituted phenylderivatives

| Compound | R | Reference |
|---|---|---|
| *Ca64* | Cl- | 12 |
| *Ca65* | Br- | 12 |
| *Ca66* | I- | 12 |
| *Ca67* | $CH_3-O-$ | 12 |
| *Ca68* | $NH_2-$ | 20, 37 |
| *Ca69* | $CH_3-\overset{\overset{O}{\|\|}}{C}-NH-$ | 20 |
| *Ca70* | $CH_3-\overset{\overset{O}{\|\|}}{C}-\overset{\overset{CH_3}{\|}}{N}-$ | 43 |
| *Ca71* |  | 20 |
| *Ca72* | $O_2N-$ | 20, 37 |
| *Ca73* |  | 33 |
| *Ca74* | $CH_3-$ | 12 |
| *Ca75* | $HO-\overset{\overset{O}{\|\|}}{C}-$ | 16 |
| *Ca76* | $CH_3-O-\overset{\overset{O}{\|\|}}{C}-$ | 16 |

| The continuation of Table 4 | | |
|---|---|---|
| *Ca77* |  | 16 |
| *Ca78* |  | 16 |
| *Ca79* |  | 29 |
| *Ca80* |  | 29 |
| *Ca81* |  | 29 |
| *Ca82* |  | 37 |
| *Ca83* |  | 25 |
| *Ca84* |  | 32 |
| *Ca85* |  | 32 |
| *Ca86* |  | 48 |

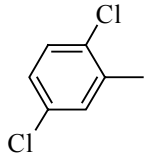
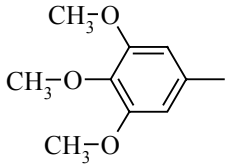
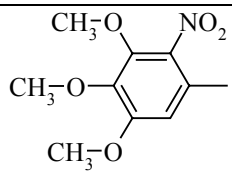
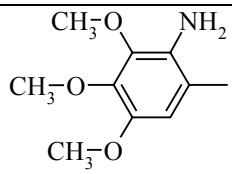
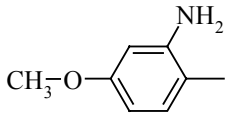
| The continuation of Table 4 | | |
|---|---|---|
| *Ca87* |  | 48 |

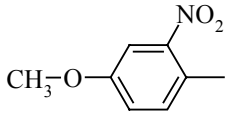
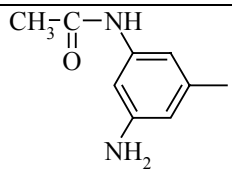
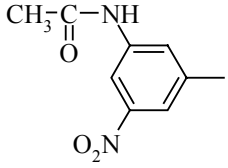
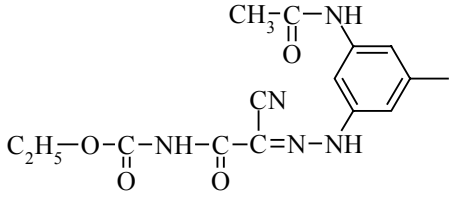
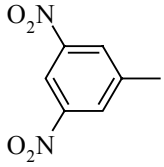
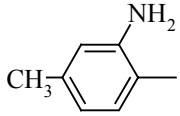
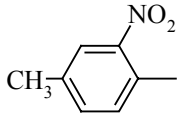
### 3.1.4. Polysubstituted phenylderivatives

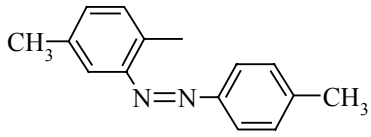
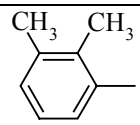
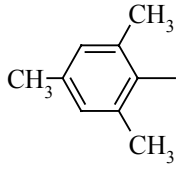
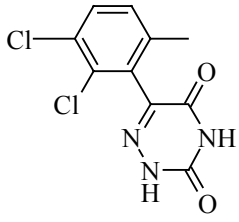
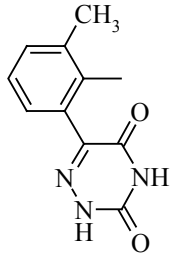
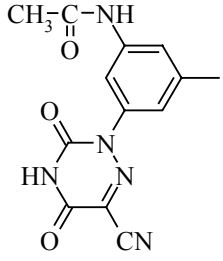


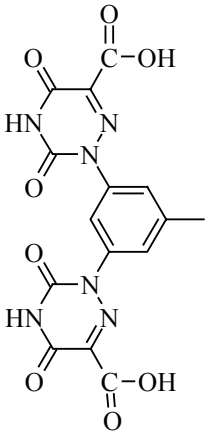
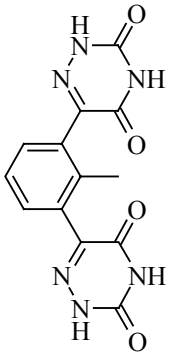
(*Ca*)

Tab. 5: Polysubstituted phenylderivatives

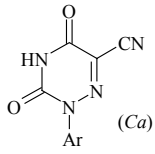
| Compound | Ar | Reference |
|---|---|---|
| *Ca88* |  | 6 |
| *Ca89* |  | 17 |
| *Ca90* |  | 95 |
| *Ca91* |  | 95 |
| *Ca92* |  | 42 |

| The continuation of Table 5 | | |
|---|---|---|
| *Ca93* |  | 42 |
| *Ca94* |  | 50 |
| *Ca95* |  | 50 |
| *Ca96* |  | 50 |
| *Ca97* |  | 47 |
| *Ca98* |  | 42 |
| *Ca99* |  | 42 |

| The continuation of Table 5 | | |
|---|---|---|
| *Ca100* |  | 33 |
| *Ca101* |  | 12 |
| *Ca102* |  | 35 |
| *Ca103* |  | 51 |
| *Ca104* |  | 45 |
| *Ca105* |  | 50 |

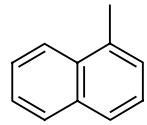
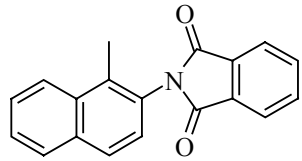
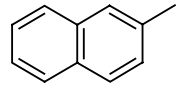
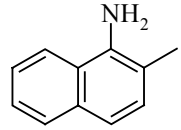
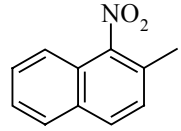
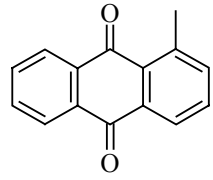
| The continuation of Table 5 | | |
|---|---|---|
| *Ca106* |  | 50 |
| *Ca107* |  | 46 |

### 3.2. Compounds containing condensed aryl rings

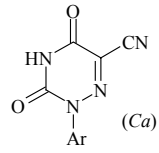


(*Ca*)

Tab. 6: Compounds containing condensed aryl rings

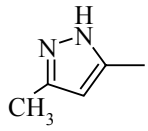
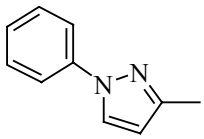
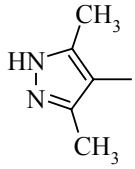
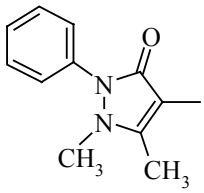
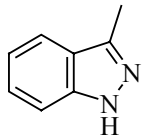
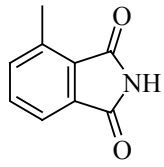
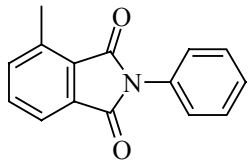
| Compound | Ar | Reference |
|---|---|---|
| *Ca108* |  | 8 |
| *Ca109* |  | 49 |
| *Ca110* |  | 8 |
| *Ca111* |  | 49 |
| *Ca112* |  | 49 |
| *Ca113* |  | 29 |

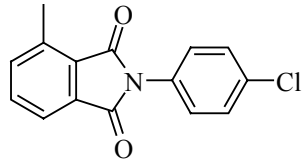
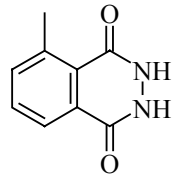
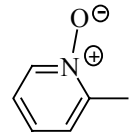
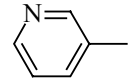
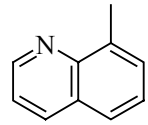
### 3.3. Compounds containing heterocyclic rings



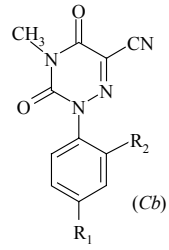
(*Ca*)

Tab. 7: Compounds containing heterocyclic rings

| Compound | Ar | Reference |
|---|---|---|
| *Ca114* |  | 15 |
| *Ca115* |  | 44 |
| *Ca116* |  | 41 |
| *Ca117* |  | 38 |
| *Ca118* |  | 19 |
| *Ca119* |  | 18 |
| *Ca120* |  | 18 |

| The continuation of Table 7 | | |
|---|---|---|
| *Ca121* |  | 18 |
| *Ca122* |  | 36 |
| *Ca123* |  | 34 |
| *Ca124* |  | 7 |
| *Ca125* |  | 24 |

### 3.4. 1-Aryl-3-methyl-6-azauracil-5-carbonitriles (Cb)



(*Cb*)

Tab. 8: 1-Aryl-3-methyl-6-azauracil-5-carbonitriles (Cb)

| Compound | $R_1$ | $R_2$ | Reference |
|---|---|---|---|
| *Cb1* | H- | H- | 60 |
| *Cb24* | $CH_3$— | H- | 60 |
| *Cb3* | Cl- | H- | 60 |
| *Cb7* | $CH_3$—O— | H- | 60 |
| *Cb8* | $C_2H_5$—O— | H- | 60 |
| *Cb68* | H- | $NH_2$— | 42 |
| *Cb72* | H- | $O_2N$— | 42 |
| *Cb98* | $CH_3$— | $NH_2$— | 42 |
| *Cb99* | $CH_3$— | $O_2N$— | 42 |
| *Cb92* | $CH_3$—O— | $NH_2$— | 42 |
| *Cb93* | $CH_3$—O— | $O_2N$— | 42 |

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## 4. References

1. Neunhoeffer H.: Chemistry of 1,2,3-triazines, 1,2,4-triazines, tetrazines and pentazines in The Chemistry of heterocyclic compounds, Vol 33. An Intersicence publication 1978, p. 264 – 330, 430 – 470.
2. Hadáček J., Slouka J.: Chemie der monocyclischen asymmetrischen Triazine, Teil I. in *FOLIA fac. sci. nat. Univ. Purkynianae Brunense* VI/3 (1965).
3. Slouka J.: *Monatsh. Chem*. **94**, 258 (1963).
4. Slouka J., Nálepa K.: *Monatsh. Chem*. **94**, 694 (1963).
5. Slouka J., Peč P.: *Monatsh. Chem*. **96**, 1874 (1965).
6. Slouka J., Nálepa K.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **18**, 253 (1965).
7. Slouka J.: *Monatsh. Chem*. **97**, 448 (1966).
8. Slouka J., Slouková I.: *Monatsh. Chem*. **97**, 1238 (1966).
9. Slouka J.: *Monatsh. Chem*. **99**, 1009 (1968).
10. Slouka J.: *Monatsh. Chem*. **100**, 342 (1969).
11. Slouka J.: *Pharmazie* **26**, 466 (1971).
12. SloukaJ., Urbanová J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **37**, 471 (1972).
13. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **37**, 477 (1972).
14. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **41**, 147 (1973); C. A. **81**, 49663e (1974).
15. Slouka J., Bekárek V., Kubatá J.: *Monatsh. Chem*. **105**, 535 (1974).
16. Slouka J., Bekárek V.: *J. prakt. Chem*. **316**, 943 (1974).
17. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **45**, 107 (1974).
18. Slouka J., Kubatý M.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **49**, 215 (1976); C. A. **87**, 68290w (1977).

19. Slouka J., Buczkowská D., Bekárek V.: *Coll. Czech. Chem. Commun*. **41**, 3090 (1976).
20. Slouka J.: *Coll. Czech. Chem. Commun*. **42**, 894 (1977).
21. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **53**, 197 (1977); C. A. **90**, 104077e (1979).
22. Slouka J.: *Pharmazie* **33**, 426 (1978).
23. Slouka J.: *Pharmazie* **34**, 796 (1979).
24. Slouka J.: *Pharmazie* **34**, 199 (1979).
25. Slouka J.: *Coll. Czech. Chem. Commun*. **44**, 2438 (1979).
26. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **61/65**, 105 (1979/1980); C. A. **94**, 192286h (1981).
27. Slouka J., Vavřín Z.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **61/65**, 117 (1979/1980); C. A. **95**, 43049b (1981).
28. Slouka J.: *Pharmazie* **35**, 744 (1980).
29. Slouka J., Bekárek V., Lyčka A: *Coll. Czech. Chem. Commun*. **47**, 1746 (1982).
30. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **79**, 39 (1984); C. A. **102**, 203946k (1985).
31. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **82**, 145 (1985); C. A. **105**, 133855r (1986).
32. Slouka J., Hejsek M.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **85**, 85 (1986); C. A. **107**, 176000s (1987).
33. Slouka J., Hejsek M.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat.* **88**, 235 (1987); C. A. **110**, 194631g (1989).
34. Slouka J., Bekárek V.: *Coll. Czech. Chem. Commun*. **53**, 626 (1988).
35. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat.* **91**, 207 (1988); C. A. **111**, 134094h (1989).
36. Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **94**, 175 (1989); C. A. **114**, 62032t (1991).
37. Slouka J.: *Coll. Czech. Chem. Commun*. **55**, 2967 (1990).
38. Slouka J., Hejsek M.: *Arch. Pharm*. **324**, 467 (1991).
39. Slouka J., Bekárek V.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **108**, 89 (1992); C. A. **119**, 49850s (1993).
40. Slouka J., Bekárek V., Hlaváč J.: *Coll. Czech. Chem. Commun*. **59**, 2741 (1994).
41. Slouka J., Rolčík J., Kameníček J., Walla J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **35**, 97 (1996); C. A. **130**, 168339w (1999).
42. Bílek P., Slouka J.: *Heter. Commun*. **4**, 325 (1998).
43. Bílek P., Slouka J.: *Heter. Commun*. **5**, 231 (1999).
44. Cankař P., Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **39**, 15 (2000); C. A. **136**, 118430c (2002).
45. Hlaváč J., Slouka J., Hradil P.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **39**, 33 (2000); C. A. **136**, 134737f (2002).
46. Hlaváč J., Slouka J., Hradil P., Lemr K.: *J. Heterocyclic Chem*. **37**, 115 (2000).
47. Bílek P., Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **40**, 7 (2001); C. A. **138**, 221555c (2003).
48. Wiedermannová I., Slouka J.: *J. Heterocyclic Chem*. **38**, 1465 (2001).
49. Bílek P., Slouka J.: *Heter. Commun*. **8**, 123 (2002).
50. Bílek P., Slouka J.: *J. Heterocyclic Chem*. **39**, 357 (2002).
51. Hlaváč J., Buchtík R., Slouka J., Hradil P., Wiedermannová I.: ARKIVOC **2003**, 22.
52. Howes H. S. jr., Koch R. C., Miller M. W.: Ger. P. 1, 951, 828; C. A. **73**, 35413m (1970).
53. Pfizer et col.: U. S. A. P. 1, 206, 698.
54. Miller M. W.: Ger. P. 2, 149, 645; C. A. **77**, 164712z (1972).
55. Miller M. W.: Ger. P. 2, 206, 395; C. A. **77**, 152237k (1972).
56. Mylari B. L.: Ger. P. 2, 230, 454; C. A. **78**, 111374e (1973).
57. Miller M. W.: U. S. A. P. 3, 912, 723; C. A. **84**, 31139r (1976).
58. Kluge A. F., Caroon J. M., Unger S. H.: *J. Med. Chem*. **21**, 529 (1978).
59. Slouka J.: *Monatsh. Chem*. **99**, 1808 (1968).
60. Slouka J., Budíková M.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. – Tom **45**, 113 (1974).
61. Whiteley M. A., Yapp D.: *J. Chem. Soc. London* **1927**, 521.
62. Slouka J., Hejsek M.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **33**, 411 (1971).

63. Slouka J., Buczkowská D.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. **57**, 187 (1978); C. A. **93**, 8138s (1980).
64. Kirti S.: Ger. P. 2, 358, 851; C. A. **81**, 77976c (1974).
65. Roesner M., Raether W.: Ger. P. 2, 722, 537; C. A. **90**, 104021g (1979).
66. Roesner M., Raether W.: S. Afr. P. 7802, 817; C. A. **91**, 157771d (1979).
67. Enders E., Haberkorn A.: Ger. P. 2, 532, 363; C. A. **86**, 190019j (1977).
68. Mylari B. L., Brenna T. M.: U. S. A. P. 3, 852, 289; C. A. **82**, 171082a (1975).
69. Brennan T. M.: U. S. A. P. 3, 883, 527; C. A. **83**, 164241n (1975).
70. Mylari B. L., Brenna T. M.: U. S. A. P. 3, 896, 172; C. A. **83**, 164299 (1975).
71. Mylari B. L.: Ger. P. 2, 430, 204; C. A. **82**, 171055d (1975).
72. Winternitz P.: *Helv. Chim. Acta* **61**, 1175 (1978).
73. Mylari B. L.: U. S. A. P. 3, 883, 528; C. A. **83**, 147506s (1975).
74. Slouka J., Stránský Z.: *Pharmazie* **28**, 309 (1973).
75. Mylari B. L.: Ger. P. 2, 428, 157; C. A. **82**, 156385b (1975).
76. Stýskala J., Slouka J., Hejsek M., Bekárek V.: *Coll. Czech. Chem. Commun*. **62**, 1754 (1997).
77. Stýskala J., Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **37**, 73 (1998); C. A. **131**, 102259g (1999).
78. Stýskala J., Slouka J.: *Heter. Commun*. **5**, 349 (1999).
79. Stýskala J., Slouka J.: *Heter. Commun*. **5**, 157 (1999).
80. Bekárek V., Slouka J.: *Coll. Czech. Chem. Commun*. **35**, 2936 (1970).
81. Bekárek V., Slouka J.: *Coll. Czech. Chem. Commun*. **39**, 566 (1974).
82. Lyčka A.: Coll. *Czech. Chem. Commun*. **49**, 2801 (1984).
83. Seifried R., Lyčka A., Bekárek V.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **41**, 49 (2002); C. A. **139**, 36208b (2003).
84. Gut J., Prystaš M., Šorm F.: *Coll. Czech. Chem. Commun*. **26**, 974 (1961).
85. Jonáš J., Gut J.: *Coll. Czech. Chem. Commun*. **27**, 716 (1962).
86. Slouka J.: *Monatsh. Chem*. **96**, 134 (1965).
87. Bílek P., Slouka J.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat. Chemica* **39**, 7 (2000); C. A. **136**, 151127z (2002).
88. Slouka J., Peč P.: *Monatsh. Chem*. **98**, 1201 (1967).
89. Slouka J., Švecová V.: *Acta Univ. Palackianae Olomucensis, Fac. Rer. Nat*. Tom **41**, 143 (1973); C. A. **81**, 49661c (1974).
90. Bougault J.: *Compt. rend*. **159**, 83 (1914).
91. Bougault J.: *Compt. rend*. **160**, 625 (1915).
92. Cattelain E.: *Bull. Soc. Chim. France* **11**, 273 (1944).
93. Hall R. H.: *J. Am. Chem. Soc*. **80**, 1145 (1958).
94. Dornow A., Menzel H., Marx P.: *Chem. Ber*. **97**, 2173 (1964).
95. Bílek P., Slouka J.: *Heter. Commun*. **10**, 67 (2004).

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Fac. rer. nat. 2004
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# SILVER COLLOIDS - METHODS OF PREPARATION AND UTILIZATION

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**Abstract**

The preparation and study of metallic particles with submicroscopic dimensions is of a recent interest in both research and technology. The reasons for this growing interest are the specific and unique properties of nanometer sized metal particles. The mentioned properties are utilized in the development and fabrication of novel biosensors, catalysts or substrates for SERS. Among the used metals the silver plays an important role; most methods of its colloid particles preparations are based on condensation methods, which are usually the reductions of the soluble silver salt. The most commonly used is the chemical reduction; both inorganic (sodium borohydride, hydrogen, hydrazine, hydrogen peroxide) and organic (citric acid, ascorbic acid, formaldehyde, reducing sugars) can be used for this purpose. Colloid silver particles can be also prepared by the action of UV or gamma radiation; in these cases the reducing agent are the reactive species (radicals, hydrated electrons) generated by the reaction mixture irradiation. Among dispersion methods of silver colloid particles preparation the most important method is the laser ablation, which yields the colloid particles of high purity.

**Key Words:** *Colloid silver, nanoparticles, preparation, SERS.*

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## Introduction

The preparation and study of metal nanoparticles is of a primary interest in both research and technology. The reason for this interest is the fact that metal nanoparticles possess specific properties not available in the cases of isolated molecules or bulk metals. These characteristic properties of the above-mentioned particles e.g. optical, magnetic, catalytic, electrochemical are dependent to a great extent on their dimensions, shape and chemical surroundings. These dependences can be advantageously utilized for the purposes of the development of novel biosensors, chemical sensors, electro optical devices, materials for high capacity data storage media[1-7] or substrates for surface enhanced Raman spectroscopy[8-13]. The metal of choice for many of the above mentioned as well as other applications is silver because of its facile preparation as well as good application properties of the silver colloidal particles.

## The formation of colloidal systems

Colloidal systems, being of transitional character between homogeneous and macroscopic heterogeneous systems can be in principle prepared by two ways – using condensation and dispersion methods. Condensation methods are based on connecting of individual atoms or molecules into larger aggregates, during the dispersion process a macroscopic phase is dispersed. A specific case of dispersion method is the peptisation based on the transition of a precipitate, which is an aggregate of colloidal particles back into colloid solution.[14]

The formation of small-sized particles via condensation mechanism is possible if sufficient amount of nuclei of a novel, thermodynamically more stable phase is formed and if the velocity of these nuclei's further growth has a suitable magnitude. The methods leading to the formation of such metastability of the systems can be (with certain restriction) divided into physicochemical and chemical. There is a vast amount of the chemical preparation methods – each reaction leading to the insoluble product formation can be employed for the purpose of a dispersion system preparation. Thus redox, hydrolytic, exchange, acidobasic and precipitation reaction can be used to obtain dispersion system.

Physicochemical methods leading to metastability of the initial system usually rely on temperature or less commonly pressure changes; a change in solvent composition is also frequently used.

Dispersing means increasing of a dispersion degree of solid or liquid materials in a dispersion environment, the result of which is the formation of a dispersion colloid having large specific interphase surface. Unlike dissolution the dispersion is usually not a spontaneous process but requires external work delivery to overcome the intermolecular forces necessary for material disintegration. Mechanical, ultrasound or laser disintegration, electric discharge sputtering belong to dispersion methods[15].

The importance of condensation methods for the preparation of dispersion systems is based on the fact that these methods can produce the finest dispersions usually impossible to be prepared by dispersion methods. Condensation methods have capability to control the dispersion degree as well as the degree of polydispersity of the

resulting colloid. The most common methods used for the preparation of colloidal suspensions of metals (silver including) are the reduction of corresponding metal cation. In addition to inorganic or organic reduction agents an ultrasound, UV radiation and gamma radiation can be used to initiate the reduction.

**Selected methods for silver particles preparation**

**1. Laser ablation**

Laser ablation of silver macroscopic material (e.g. silver foil) is a novel and promising physical method for the silver colloid particles preparation. The advantages of this method are namely an ease of the process, versatility with regard to metal identity or choice of solvent as well as the absence of additive chemical agents residues.[16] Metal particles prepared by laser ablation are chemically pure and therefore suitable for the use in SERS[17-21] as the presence of residual ions at the surface of colloidal particles significantly affects the absorption processes, particle stability and reproducibility of SERS measurement. For the purposes of SERS measurement not only the colloidal particles formed by laser ablation, but also the silver foil remaining after the process can be used[16]. The size of the silver particles prepared by this method ranges from nanometer sizes up to 30-40 nm and depends on wavelength and intensity of the laser used, on irradiation time,[22] presence of chlorides[18] or surfactants[23] and the solvent in which the irradiation is carried out[22].

**2. The reduction by the action of ultrasound**

Except for the above-mentioned usage of ultrasound in a dispersion method of colloid particle preparation it can be used also as a condensation method. The ultrasound is capable to decompose water into hydrogen and hydroxyl radicals. Subsequent reactions with suitable additives yield organic radicals which act as reducing agents. By sonification of aqueous silver salts solutions in the presence of surfactants (the frequency of ultrasound was 200 kHz) the silver particles of 13±3 nm size were prepared[24].

**3. The reduction by the action of gamma radiation**

For the preparation of submicroscopic silver particles a direct radiolysis of silver salt aqueous solutions can be used. The advantage of this preparation method is that minimum interfering chemical substances are introduced into the reaction mixture, which could possibly absorb onto particles and thus change their specific properties. During the irradiation of silver salt solution under hydrogen gas atmosphere hydrated electrons and hydrogen atoms are formed, which reduce the silver ions. Concomitantly OH radicals, which oxidise silver particles, are formed. In the presence of hydrogen gas a part of OH radicals reacts with hydrogen molecule yielding hydrogen atoms, which contribute to silver ion reduction. By the action of this simultaneous silver ions reduction/silver particles oxidation a gradual growth is achieved, the structural defects

are therefore minimised and almost monodisperse particles with average size of 7.0 nm are prepared[25]. The course of the reduction by gamma irradiation can be influenced by other chemical agents, e. g. 2-propanol[26]. The binding of silver ions into complex with appropriate complex agent can be the other factor usable for the influence of the reduction by gamma irradiation[27].

**4. The reduction by the action of UV radiation**

Photochemical method of colloid particle preparation using UV radiation yields the particles with properties similar to the particles produced by the above mentioned radiolytic method, its advantage being the simpler and cost effective experimental equipment. Mercury discharge lamp is often used as the source of UV radiation. In addition to silver salt and eventual stabilisers the reaction mixture contains suitable organic substance whose interaction with UV radiation generates radicals which reduce silver ions[28-31]. The example of this method can be demonstrated by the system containing except for $AgClO_4$ an acetone, 2-propanol and polymeric stabilisers (polyethyleneimine, sodium polyphosphate, sodium polyacrylate and polyvinylpyrrolidone). Acetone is excited by the absorption of UV radiation; the excited state reacts with 2-propanol yielding strongly reducing ketyl radicals. With polyethyleneimine as stabiliser the particles with narrow size distribution and 7 nm mean size were prepared[28]. Acetophenon[29], benzophenon[30] or ascorbic acid[31] can be used as photosensitive agent instead of acetone.

**5. The reduction by inorganic agents**

The most commonly used method for the preparation of silver sols is the reduction of silver salt by sodium borohydride, usually following the manuscript proposed by Creighton et al.[8], frequently used especially in the area of SERS[8-10,32-35]. The procedure after Creighton et al. is based on the addition of 25 ml of $AgNO_3$ ($10^{-3}$ mol.dm$^{-3}$) aqueous solution into 75 ml of the intensively stirred, ice cooled aqueous $NaBH_4$ ($10^{-3}$ mol.dm$^{-3}$) solution. Since the time of publication many modifications of Creighton procedure differing in the concentrations and molar ratios of the reactants appeared. Among other factors investigated which influence the reduction of silver salt by $NaBH_4$ are the temperature[36], the presence of surfactants[37], the presence of nonsaturated carboxylic acids[38], the presence of $NaHCO_3$, the exchange of $H_2O$ for $D_2O$[39] or the method of stirring[30]. By the standard methods of silver salt reduction by $NaBH_4$ the particles with units of nanometers sizes and narrow size distributions are prepared, however the preparations of larger particles is difficult. A modification for larger silver particles preparation was proposed by Schneider et al., in this modifications small particles are prepared by the reduction using $NaBH_4$ and are subsequently used as nuclei for further growth in which „weaker“ reducing agents is used (ascorbic acid)[40]. Colloid silver can be also prepared by the reduction by hydrazine or hydrogen, depending on the experimental procedure used the silver particles with sizes ranging from units of nanometers[41] up to several tenths of nanometers[42] are obtained. Basic solution of hydrogen peroxide can also be used[43]. There are a useful method of preparation of silver

colloid by the reduction of silver salt solution by the complex compounds of ferrous salt[44].

### 6. The reduction by organic reducing agents

Among reduction by organic substances the citrate reduction procedure according to Lee-Meisel[45] is one of the most commonly used, especially for the purposes of SERS[11,12,46-56]. Silver sol is prepared by the addition 10 ml of 1% trisodium citrate into 500 ml of aqueous solution containing 90 mg of $AgNO_3$. The reaction mixture is kept boiling for one hour. It was shown by spectroscopic techniques that the reduction of silver ions occurs during first two minutes after the addition of citrate, the primary particles are relatively large and polydisperse (60 – 80 nm). Subsequent heating of the reaction mixture leads to monodisperse particles with 27 nm average size[57]. The reduction process can be carry out as two stage process, the particles created in the first step can serve as the nuclei for the further growth[58]. The silver particles can be obtained also by the well known Tollens reagent - the silver ions in the form of ammonium complex being reduced by aldehydes or reducing sugars. Formaldehyde and sorbitol used as reducing agents give the particles with the sizes ranging from 20 to 50 nm.[59] Colloid silver can be prepared also using ascorbic acid to reduce aqueous $AgNO_3$ solution. In the presence of the vinylalcohol and N-vinylpyrrolidone copolymer as additives the particles with resulting size from 3-7 nm were prepared depending on the amount of the added polymer[60].

In nonaqueous medium the solvent can serve as the reducing agent – e.g. N,N-dimethylformamide[61-63], dimethylsulfoxide[64] or 2-propanol[60]. The dimensions of the resulting silver particles range from several units of to twenty nanometers.

## The selected examples of silver colloids‘ applications

### 1. Surface enhanced Raman spectroscopy and surface enhanced resonance Raman spectroscopy

The detection of very low concentrations of chemical substances in the solutions is necessary and important in many fields of the human activity – chemistry, biology, medicine, pharmacy etc.[46,65,66]

The surface enhanced Raman scattering (SERS) and especially the surface enhanced resonance Raman scattering (SERRS) are the sensitive spectroscopic techniques whose potential for the trace analysis is recently actively investigated[67,68]. When SERS and SERRS especially is used as an analytical method the detection limits comparable to fluorescence spectroscopy can be achieved with more structural information in the same analysis time[48,69]. The detection limit of SERS and SERRS lies in piko to femtomolar concentrations[48]. Recently the detection of a single molecule has been achieved using SERS[48,68,69].

For the purposes of the SERS and SERRS analysis a range of metals (e.g. Ag, Au, Cu, Al, V, Li, and Na) was tested in the form of colloidal suspensions, paper based films, silica or Teflon particles. It was found that noble metals (Ag, Au, Cu)[69] are suitable materials when visible spectral region lasers are used, the most commonly used

metal is silver[65-69]. Some works suggest that only a very small fraction of silver colloid particles possess extremely high effectivity of enhancement. These particles are called „the hot particles“ and their real SERS enhancement factors can exceed $10^{14}$ až $10^{15}$, such enhancement corresponds to the cross section ca $10^{-15}$ $cm^2$ per molecule[70]. Such a high magnitude of Raman scattering enables the detection, identification and dynamic study of a single molecule adsorbed on a single colloid particle[48,68-75]. It was found using the microscopic technique that the size of these hot particles ranges from 80 to 100 nm[73]. Enhancement factor depends on the shape of particles too.

## 2. Catalytic properties

The metal colloid dispersions are commonly used as the reduction catalysts, but are rarely used as the catalysts for oxidation. The colloid silver is the exception, it is often used as the oxidation catalyst e.g. in the process of the preparation of ethylene oxide from ethylene[76,77].
Redox properties of small metallic particles differ from these properties of the bulk metal. The experiments carried out with the commonly used metals (Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Pt, Au, Hg) proved that their catalytic properties are dependent on the particle size.[78] The research in the area of the small metal particles' redox properties is focused mainly on the stable particles in the final stage of their growth, the reports of the growing particles‘ redox properties are scarce. During the growth of these small particles possessing renewing surface of extremely large area with excellent catalytic properties a smooth change of their redox potentials occurs[78,79].

## 3. The use of silver particles in sensorics

The optical response of noble metal nanoparticles is often characterized by the presence of a strong absorption band that is absent from the spectrum of the bulk metal. This is attributed to a resonance in the collective motion (oscillation) of the conduction electrons in response to an incident electromagnetic field and is called the surface plasmon resonance (SPR)[2,80]. The localisation of peak absorption wavelength $\lambda_{max}$ and shape of the band depends on the particle size and shape, on the degree of their mutual interactions, and local external dielectric environment. This dependence can be utilized for the development of a new class of high sensitive sensors. For example the $\lambda_{max}$ peak of the surface plasmon resonance of the biotin-functionalised triangular silver nanoparticles is highly sensitive towards the chemical surroundings of the particle. Exposure of these nanoparticles to 100 $nmol.dm^{-3}$ streptavidin caused a 27 nm red-shift in $\lambda_{max}$. The detection limit of this sensor lie in the range of $10^{-12}$ – $10^{-13}$ $mol.dm^{-3}$ and prospect new ways into an ultrasensitive analysis with low requirements on the laboratory equipment[81].

## 4. Antimicrobial activity of colloid silver

The antimicrobial activity of silver is known for a long time. Since the times of antient Greece and Rome the silver vessels were used for the conservation of water and

other liquids to ensure their health safety. In middle age the powder silver was used as the food additive. However in this form the silver is not biologically well consumable and the symptoms of silver poisoning appeared after some time (argyria)[82].

In the course of nineteenth and especially at the beginning of the twentieth centuries the silver colloid particles attracted the attention of microbiology and medicine. The study of antimicrobial properties of these particles however ceased because of the invention of antibiotics which took-over the leading position in the „fight against bacteria".

Recently the resistance of bacteria against antibiotics increases however most of microorganisms are unable to develop the self-defendence against the colloid silver[83]. The mechanism of the silver antimicrobial activity is yet not known in detail[84]. The optimum antimicrobial effect provide the silver colloid particles with 1 – 10 nm size[83,85].

## Conclusion

From the above-mentioned list of the silver colloid particles' applications implies the necessity of further development of the preparation methods, focused on the design of the particles with desired properties according to the requirements of the specific application. Up to now number of published methods have only limited capabilities to influence even the most basic properties of the particles – their shape, dimensions and polydispersity, their surface charge and in the case of larger particles the stability in dispersion. The further development of the silver colloid particles preparation (and in the preparations of other metal particles, which encounter similar problems as well) will therefore focus on the synthesis of silver nanoparticles of desired size and shape according to the application requirements. Some possibilities already exist in influencing the size of the silver colloid particles. Except the already mentioned secondary enlargement of the particle sizes in the second reduction step[40,58] it is possible to utilise binding of the silver ions into complex compound[86]. The magnitude and the sign of the surface charge of the prepared colloid particles can be influenced by the addition of a suitable surface active agent[87], their stability can be influenced by the addition of macromolecular substances. However there are many more possible ways of the colloid silver particles, new possibilities appear in the case of dispersion methods, especially promising is the laser ablation. Most probably the near future will bring the rapid development of the preparation methods, which will enable the further progress in the application possibilities of the colloid particles of silver and other metals as well.

## References


1. Riboh J. C., Haes A. J., McFarland A. D., Yonzon C. R. and Van Duyne R. P.: *J. Phys. Chem. B* **107**, 1772 (2003).
2. Malinsky M. D., Kelly K. L., Schatz G. C. and Van Duyne, R. P.*: J. Am. Chem. Soc.* **123**, 1471 (2001).
3. Zynio S. A., Samoylov A. V., Surovtseva E. R., Mirsky V. M. and Shirshov Y. M. J.: *Sensors* **2**, 62 (2002).
4. Hulteen J. C., Treichel D. A., Smith M. T., Duval M. L., Jensen T. R. and Van Duyne R. P.: *J. Phys. Chem. B* **103**, 9846 (1999).

5. Henry A. C. and McCarley R. L.: *J. Phys. Chem. B* **105**, 8755 (2001).
6. Fuller S. B., Wilhelm E. J. and Jacobson J. M.: *J. Microelctromech. Syst.* **11**, 54 (2002).
7. Yin Y., Lu Y., Sun Y., Xia Y.: *Nano Lett.* **2**, 427 (2002).
8. Creighton J. A., Blatchford C. G. and Albrecht M. G.: *J. Chem. Soc., Faraday Trans. 2* **75**, 790 (1979).
9. Laserna J. J., Cabalin L. M. and Montes R.: *Anal. Chem.* **64**, 2006 (1992).
10. Vlčková B., Solecká-Čermáková K., Matějka P. and Baumruk V.: *J. Mol. Struct.* **408/409**, 149 (1997).
11. Félidj N., Aubard J. and Lévi G.: *Phys. Stat. Sol. (A)* **175**, 367 (1999).
12. Feng Z. C., Liang C. H., Li M. J. and Chen J., Li C.: *J. Raman Spectrosc.* **32**, 1004 (2001).
13. Etchegoin P., Liem H., Maher R. C., Cohen L. F., Brown R. J. C., Milton M. J. T. and Galop J. C.: *Chem. Phys. Lett.* **367**, 223 (2003).
14. Handbook of applied Surface and Colloid Chemistry, Vol. 2, Ed. Krister Holmberg, John Wiley and Sons, Ltd., Chichester 2002, p. 3.
15. Hunter R. J.: *Foundations of colloidal science*. Oxford University Press, Oxford 2001.
16. Lee I., Han S. W. and Kim K.: *J. Raman Spectrosc.* **32**, 947 (2001).
17. Smejkal P., Vlčková B., Procházka M., Mojzeš P. and Pfleger J.: *J. Mol. Struct.* **483**, 225 (1999).
18. Procházka M., Mojzeš P., Štěpánek J., Vlčková B. and Turpin P.-Y.: *Anal. Chem.* **69**, 5103 (1997).
19. Srnová I., Procházka M., Vlčková B., Štěpánek J. and Malý P.: *Langmuir* **14**, 4666 (1998).
20. Mafuné F., Kohno J., Takeda Y. and Kondow T.: *J. Phys. Chem. B* **104**, 9111 (2000).
21. Tsuji T., Kakita T. and Tsuji M.: *Appl. Surf. Sci.* **206**, 314 (2003).
22. Jeon J. S. and Yeh C. S.: *J. Chin. Chem. Soc.* **45**, 721 (1998).
23. Chen Y. H. and Yeh C. S.: *Colloid Surf. A-Physicochem. Eng. Asp.* **197**, 133 (2002).
24. Nagata Y., Watananabe Y., Fujita S., Dohmaru T. and Taniguchi S.: *J. Chem. Soc., Chem. Commun.* 1620 (1992).
25. Gutiérrez M. and Henglein A.: *J. Phys. Chem* **97**, 11368 (1993).
26. Henglein A. and Giersig M.: *J. Phys. Chem. B* **103**, 9533 (1999).
27. Henglein A.: *Langmuir* **17**, 2329 (2001).
28. Henglein A.: *Chem. Mater.* **10**, 444 (1998).
29. Sato T., Onaka H. and Yonezawa Y.: *J. Photochem. Photobiol. A–Chem.* **127**, 83 (1999).
30. Kapoor S.: *Langmuir* **14**, 1021 (1998).
31. De S., Pal A., Jana N. R. and Pal T.: *J. Photochem. Photobiol. A–Chemistry* **131**, 111 (2000).
32. Lecomte S., Matejka P., and Baron M. H.: *Langmuir* **14**, 4373 (1998).
33. Muniz-Miranda M.: *J. Raman Spectrosc. B* **33**, 295 (2002).
34. Muniz-Miranda M.: *J. Phys. Chem. A* **101**, 7803 (2000).
35. Sanchez-Cortes S., Garcia-Ramos J. V.: *Surf. Sci.* **473**, 133 (2001).
*36.* Van Hyning D. L. and Zukoski C. F.: *Langmuir* **14**, 7034 (1998).
37. Pal T., Sau T. K. and Jana N. R.: *J. Colloid Interface Sci.* **202**, 30 (1998).
38. Wang W., Chen X. and Efrima S.: *J. Phys. Chem. B* **103**, 7238 (1999).
39. Teiten B. and Burneau A.: *J. Colloid Interface Sci.* **206**, 267 (1998).
40. Schneider S., Halbig P., Graen H. and Nickel U.: *Photochem. Photobiol.* **60**, 605 (1994).
41. Nickel U., zu Castell A., Pöppl K. and Schneider S.: *Langmuir* **16**, 9087 (2000).
42. Esumi K., Ishizuki N., Torigoe K., Nakamura H. and Meguro K.: *J. Appl. Polym. Sci.* ***44***, 1003 (1992).
43. Li Y. S., Cheng J. C. and Coons L. B.: *Spectroc. Acta Pt. A–Molec. Biomolec. Spectr.* **55**, 1197 (1999).
44. Silman O., Bumm L. A., Callaghan R., Blatchford C. G. and Kerker M.: *J. Phys. Chem.* **87**, 1014 (1983).
45. Lee P. C. and Meisel D.: *J. Phys. Chem.* **86**, 3391 (1982).
46. Graham D., Smith W. E, Linacre A. M. T., Munro C. M., Watson N. D. and White P. C.: *Anal. Chem.* **69**, 4703 (1997).
47. Kneipp K., Wang Y., Dasari R. R. and Feld M. S.: *Appl. Spectrosc.* **49**, 780 (1995).
48. Maruyama Y., Ishikawa M. and Futamata M.: *Chem. Lett.* 834 (2001).
49. Maxwell D. J., Emory S. R. and Nie S. M.: *Chem. Mater.* **13**, 1082 (2001).
50. Eggeling C., Schaffer J., Seidel C. A. M., Korte J., Brehm G., Schneider S. and Schrof W.: *J. Phys. Chem. A* **105**, 3673 (2001).
51. Cinta-Pinzaru S., Cavalu S., Leopold N., Petry R. and Kiefer W.: *J. Mol. Struct.* **565**, 225 (2001).
52. Rivas L., Sanchez-Cortes S. and Garcia-Ramos J. V.: *Phys. Chem. Chem. Phys.* **4**, 1943 (2002).
53. Prochazka M., Stepanek J., Turpin P. Y. and Bok J.: *J. Phys. Chem. B* **106**, 1543 (2002).
54. Pavel I., Moigno D., Cinta S. and Kiefer W.: *J. Phys. Chem. B* **106**, 3337 (2002).
55. Keating C. D., Kovaleski K. K. and Natan M. J.: *J. Phys. Chem. B* **102**, 9414 (1998).

56. Liang E. J., Ye X. L. and Keifer W.: *J. Phys. Chem. A* **101**, 7330 (1997).
57. Munro C. H., Smith W. E., Garner M., Clarkson J. and White P. C.: *Langmuir* **11**, 3712 (1995).
58. Rivas L., Sanchez-Cortes S., Garcia-Ramos J. V. and Morcillo G.: *Langmuir* **17**, 574 (2001).
59. Yin Y. D., Li Z. Y., Zhong Z. Y., Gates B., Xia Y. N. and Venkateswaran S.: *J. Mater. Chem.* **12**, 522 (2002).
60. Huang Z.-Y., Mills G. and Hajek B.: *J. Phys. Chem* **97**, 11542 (1993).
61. Pastoriza-Santos I. and Liz-Marzan L.: *Langmuir* **15**, 948 (1999).
62. Pastoriza-Santos I. and Liz-Marzan L. M.: *Pure Appl. Chem.* **72**, 83 (2000).
63. Pastoriza-Santos I. and Liz-Marzan L. M.: *Langmuir* **18**, 2888 (2002).
64. Rodriguez-Gattorno G., Diaz D., Rendon L. and Hernandez-Segura G. O.: *J. Phys. Chem. B* **106**, 2482 (2002).
65. Wang Y., Li Y. S., Zhang Z. X. and An D. Q.: *Spectroc. Acta Pt. A-Molec. Biomolec. Spectr.* **59**, 589 (2003).
66. Vankeirsbilck T., Vercauteren A., Baeyens W., Van der Veken G., Verpoort F., Vergote G. and Remon J. F.: *Trac-Trends Anal. Chem.* **21**, 869 (2002).
67. Isola N. R., Stokes D. L. and Vo-Dinh T.: *Anal. Chem.* **70**, 1352 (1998).
68. Jones J. C., McLaughlin C., Littlejohn D., Sadler D. A., Graham D. and Smith W. E.: *Anal. Chem.* **71**, 596 (1999).
69. Garrell R. L.: *Anal. Chem.* **61**, 401 (1989).
70. Emory S. R., Haskins W. E. and Nie S.: *J. Am. Chem. Soc.* **120**, 8009 (1998).
71. Doering W.E. and Nie S. M.: *J. Phys. Chem. B* **106**, 311(2002).
72. Kneipp K., Wang Y., Kneipp H., Perelman L. T., Itzkan I., Dasari R. R. and Feld M. S.: *Phys. Rev. Lett.* **78**, 1667 (1997).
73. Nie S. and Emory S. R.: *Science* **275**, 1102 (1997).
74. Bizzarri A. R. and Cannistraro S.: *Appl. Spectrosc.* **56**, 1531 (2002).
75. Pettinger B., Picardi G., Schuster R. and Ertl G.: Electrochemistry *68*, 942 (2000).
76. Shiraishi Y. and Toshima N.: *J. Mol. Catal. A–Chemical* **141**, 187 (1999).
77. Shiraishi Y. and Toshima N.: *Colloid Surf. A–Physicochem. Eng. Asp.* **169**, 59 (2000).
78. Jana N. R. and Pal T.: *Curr. Sci.* **75**, 145 (1998).
79. Jana N. R., Sau T. K. and Pal T.: *J. Phys. Chem. B* **103**, 115 (1999).
80. Englebienne P., Van Hoonacker A. and Verhas M.: *Spectr. – Int. J.* **17**, 255 (2003).
81. Haes A. J. and Van Duyne R. P.: *J. Am. Chem. Soc.* **124**, 10596 (2002).
82. http://www.thehealthstore.com/silver.html
83. http://www.silver-colloids.com
84. Keleher J., Bashant J., Heldt N., Johnson L. and Li Y.: *World J. Microbiol. Biotechnol.* **18**, 133 (2002).
85. Lee H. J., Yeo S. Y. and Jeong S. H.: *J. Mater. Sci.* **38**, 2199 (2003).
86. Kvítek L., Prucek R., Pikal P. and Novotný R.: *Acta Univ. Palacki. Olom. Chemica* **38**, 33 (1999).
87. Kvítek L., Prášková M., Pikal P., Prucek R. and Novotný R.: *Acta Univ. Palacki. Olom. Chemica* **40**, 41 (2001).

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# DIBENZYL AND BENZYLBUTYL DITHIOCARBAMATES OF NICKEL(II) WITH P-LIGANDS

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**Abstract**

Some novel Ni(II) dithiocarbamates with P ligands have been prepared. Syntheses arose from $[Ni(Bz_2dtc)_2]$ and eventuated in following complexes: $[NiX(Bz_2dtc)(PR_3)]$ and $[Ni(Bz_2dtc)(PPh_3)_2]Y$; complex type $[NiX(BzButdtc)(PBu_3)]$ was synthesised too (Bz = benzyl; Bu = butyl; dtc = $S_2CN$; X = Cl, Br, I, NCS; R = phenyl, butyl; Y = $ClO_4$ and $PF_6$). Obtained compounds have been characterised by elemental analysis, IR and UV/VIS spectroscopy, magnetochemical and conductivity measurements and also by melting points. The used methods have indicated that the compounds are diamagnetic, non-electrolytes except (**IX**-**X**) (1:1 electrolytes) with square planar $NiS_2PX$ or $NiS_2P_2$ (**IX**-**X**) chromophores.

**Key Words:** *Nickel(II) dithiocarbamate complexes; P-ligands; synthesis; physico-chemical study*

## Introduction

Within the framework of our quest for new Ni(II) dithiocarbamates with P ligands in the coordination sphere, some new compounds have been prepared. This type of compounds was studied not only by our department and also by authors.[1-15] X-ray structure analyses of $[NiCl(Et_2dtc)(PPh_3)]$[5,7], $[Ni(NCS)(Bu_2dtc)(PEt_3)]$[8], $[NiI(Am_2dtc)(PPh_3)]$[11] (Et = ethyl, Ph = phenyl, Bu = butyl, Am = amyl, dtc = $S_2CN$)

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confirmed distorted square coordination of $NiS_2PX$ polyhedron (X = Cl, N, I). Compounds with $NiS_2P_2$ chomophore, such as $[Ni(Et_2dtc)(PPh_3)_2]ClO_4$[6], $[Ni(i\text{-}Pr_2dtc)(PPh_3)_2]ClO_4 \cdot CHCl_3$[9] (*i*-Pr = isopropyl) and $[Ni(Am_2dtc)(PPh_3)_2]ClO_4$[11] were also studied by X-ray structure analyses that confirmed a distorted square arrangement around nickel atom in these compounds. Similar data were obtained for non-symmetrical dithiocarbamates (with $R_1R_2dtc$, $R_1 \neq R_2$).[15,16]

No data for Ni(II) di(benzyl)dithiocarbamates and Ni(II) benzylbutyldithiocarbamates with P-ligands have been reported. The main purpose of this work was the synthesis and physico-chemical characterization of these compounds.

## Materials and methods

Di(benzyl)amine (97%), benzylbutylamine (98%), $LiClO_4 \cdot 3H_2O$, $PPh_3$ and $PBu_3$ were purchased from Aldrich Co., $CS_2$ and $K[PF_6]$ from Fluka Co. All other chemicals were obtained from Lachema Co.

Nickel content was determined by chelatometric titration[17] and chlorine (bromine) by the Schöniger method.[18] C, H, N and S analyses were performed on an EA 1108 instrument (Fisons). Room temperature magnetic susceptibilities were measured by the Faraday method using $Co[Hg(NCS)_4]$ as calibrant on a laboratory-designed instrument employing a Sartorius 4434 MP-8 microbalance. Conductivities were measured with a Conductivity Hand-Held Meter LF 330 (WTW GmbH) at 25°C. Diffuse-reflectance electronic spectra (45000 – 11000 $cm^{-1}$) were obtained by a Specord M 40 and IR spectra (4000 – 400 $cm^{-1}$) by a Specord M 80 (Carl Zeiss, Jena) using nujol mulls. The melting points were determined on a Boëtius instrument (VEB Wägetechnik Rapido, PHMK 79/2122).

## Syntheses of compounds

$[NiX(Bz_2dtc)(PR_3)]$ (X = Cl, Br, I, NCS; R = phenyl, butyl)

The compounds were obtained by the reaction of a suspension of finely powdered complexes $[Ni(Bz_2dtc)_2]$[19] (1 mmol) and $[NiX_2(PR_3)_2]$[20] (1 mmol), in chloroform (10 $cm^3$). The mixture was properly stirred (2 hours) and after filtration the solutions were left to crystallize at room temperature. For complex of the $[NiX(Bz_2dtc)(PPh_3)]$ type, mixtures of green powder $[Ni(Bz_2dtc)_2]$ and novel compound formed; the mixtures were dissolved in $CHCl_3$ and after filtration left to crystallize at room temperature. Resulted violet (red, orange) powders were dried at room temperature. The same method was used for $[NiCl(Bz_2dtc)(PBu_3)]$, but complexes $[NiBr(Bz_2dtc)(PBu_3)]$ and $[Ni(NCS)(Bz_2dtc)(PBu_3)]$ were only washed with diethyl ether and *n*-hexane, dried at room temperature and powdered.

[NiX(BzButdtc)($PBu_3$)] (X = Cl, Br, NCS)

A suspension [Ni(BzBudtc)$_2$][16] (1 mmol) and [$NiX_2(PBu_3)_2$][20] (1 mmol) in chloroform (25 $cm^3$) was thoroughly stirred (30 minutes). Reaction eventuated in solutions, which were filtered and left to crystallize at room temperature. Products were washed with petrol ether and dried by using an IR-lamp at 40°C.

[Ni($Bz_2dtc$)($PPh_3$)$_2$]Y (Y = $ClO_4$ and $PF_6$)

A suspension of powdered [Ni($Bz_2dtc$)$_2$] (1 mmol), $PPh_3$ (2 mmol) and $NiCl_2 \cdot 6H_2O$ (1 mmol) in methanol (25 $cm^3$) was stirred under reflux. After 1 hour, powdered $LiClO_4 \cdot 3H_2O$ (1 mmol) or K[$PF_6$] (1 mmol) was added and the mixture was refluxed for 1 hour. Resulted red powders were filtered, washed with $CHCl_3$ and diethyl ether and dried at room temperature.

## Results and discussion

Chemical formulas and analytical data for all these compounds are given in Table 1; results of physico-chemical studies are mentioned in Table 2.

It was found that all compounds are diamagnetic. [Ni($Bz_2dtc$)$_2$], [NiX($Bz_2dtc$)($PR_3$)] and [NiX(BzButdtc)($PBu_3$)] are non-electrolytes; [Ni($Bz_2dtc$)($PPh_3$)$_2$]Y (Y = $ClO_4$, $PF_6$) are 1:1 electrolytes.[21] This is consistent with assumption of a square planar arrangement of $NiS_4$, $NiS_2PX$ and $NiS_2P_2$. Ionic character of Y in [Ni($Bz_2dtc$)($PPh_3$)$_2$]Y is indicated by IR spectroscopy: a singlet $\nu_3$ at 1090 $cm^{-1}$ and $\nu_4$ at 620 $cm^{-1}$ for $ClO_4$ group[22] and single vibration at 840 $cm^{-1}$ for $PF_6$[23] were found. Complexes **V**, **VIII** and **XIII** with NCS anion exhibit coordination of this group to the nickel atom via nitrogen[24]: $\nu$(C≡N) is in the range 2100-2080 $cm^{-1}$ and $\nu$(C-S) is for all complexes discussed at 840 $cm^{-1}$.

IR spectra of all reported compounds exhibit $\nu$(C···N) and $\nu$(C···S) vibrations at 1520-1495 $cm^{-1}$ and 1010-990 $cm^{-1}$ typical for dithiocarbamate complexes.[25,26] Square planar coordination is supported by electronic spectroscopy results: bands in the 15800-25800 $cm^{-1}$ region are typical of square planar Ni(II) compounds.[27,28] Bands above 30000 $cm^{-1}$ are likely connected with intra-ligand transitions in the $S_2CN$ group.[29]

Proposed structure formulas of prepared complexes based on literature data listed above and our experimental results are given in figures 1 and 2.

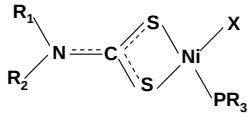


**Fig. 1.** Predicted structural formula for the complexes of [NiX($Bz_2dtc$)($PR_3$)] and [NiX(BzButdtc)($PBut_3$)] types (X = Cl, Br, I, NCS; R = phenyl, butyl)

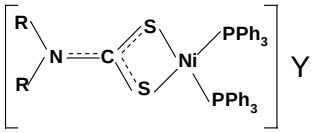


**Fig. 2.** Predicted structural formula for the complexes of $[Ni(Bz_2dtc)(PPh_3)_2]Y$ type (R = benzyl, Ph = phenyl, Y = $ClO_4$ or $PF_6$)

## **Table 1.** Elemental analyses

| Compound | | Found/Calcd. (%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | Ni | C | H | N | S | Cl (Br) |
| **I** | $[Ni(Bz_2dtc)_2]$ | 10.3/9.7 | 59.3/59.7 | 4.6/4.7 | 4.7/4.6 | 20.5/21.3 | - |
| **II** | $[NiCl(Bz_2dtc)(PPh_3)]$ | 9.4/9.3 | 62.3/63.0 | 4.8/4.7 | 2.4/2.2 | 9.4/10.2 | 6.1/5.6 |
| **III** | $[NiBr(Bz_2dtc)(PPh_3)]$ | 9.0/8.7 | 58.6/58.9 | 4.4/4.3 | 2.2/2.1 | 9.0/9.5 | 12.6/11.9 |
| **IV** | $[NiI(Bz_2dtc)(PPh_3)]$ | 8.6/8.2 | 54.6/55.0 | 4.1/4.1 | 2.0/1.9 | 7.5/8.9 | - |
| **V** | $[Ni(NCS)(Bz_2dtc)(PPh_3)]\cdot CHCl_3$ | 8.0/7.6 | 55.3/54.5 | 3.5/3.9 | 3.7/3.6 | 12.5/12.5 | 12.9/13.8 |
| **VI** | $[NiCl(Bz_2dtc)(PBut_3)]$ | 9.7/10.3 | 56.1/57.0 | 7.9/7.3 | 2.3/2.5 | 8.8/11.3 | 5.5/6.2 |
| **VII** | $[NiBr(Bz_2dtc)(PBut_3)]$ | 9.9/9.6 | 51.7/52.3 | 7.1/6.7 | 2.3/2.3 | 7.2/8.2 | 13.5/13.0 |
| **VIII** | $[Ni(NCS)(Bz_2dtc)(PBut_3)]$ | 10.3/9.9 | 55.7/56.9 | 7.8/7.0 | 4.8/4.7 | 15.7/16.3 | - |
| **IX** | $[Ni(Bz_2dtc)(PPh_3)_2]ClO_4$ | 6.4/6.2 | 63.4/64.1 | 4.4/4.6 | 1.4/1.5 | 6.2/6.7 | 4.2/3.7 |
| **X** | $[Ni(Bz_2dtc)(PPh_3)_2]PF_6$ | 5.8/5.9 | 60.3/61.2 | 4.1/4.4 | 1.4/1.4 | 5.4/6.4 | - |
| **XI** | $[NiCl(BzButdtc)(PBut_3)]$ | 10.6/11.0 | 54.2/53.9 | 8.2/8.1 | 2.6/2.6 | 12.3/12.0 | 5.9/6.6 |
| **XII** | $[NiBr(BzButdtc)(PBut_3)]$ | 10.3/10.1 | 49.3/49.8 | 7.6/7.5 | 2.6/2.4 | 11.0/11.1 | 14.2/13.8 |
| **XIII** | $[Ni(NCS)(BzButdtc)(PBut_3)]$ | 10.6/10.5 | 53.6/53.9 | 7.8/7.8 | 5.1/5.0 | 17.3/17.3 | - |

## **Table 2.** Physico-chemical study

| Compd. | Colour | Yield (%) | $\lambda_M$[a] [$Scm^2mol^{-1}$] | IR [$cm^{-1}$][c] ν(C⋯S) | ν(C⋯N) | | UV/VIS[c] [$10^3$ $cm^{-1}$] | $T_t$ [°C] |
|---|---|---|---|---|---|---|---|---|
| **I** | green | 80 | 1.1 | 990 m | 1495 s | - | 15.8; 20.5; 24.4; 25.8 | 241 |
| **II** | violet | 38 | 2,1 | 995 m | 1500 m | - | 19.2; 29.5 | 188 |
| **III** | violet | 41 | 2.6 | 995 m | 1500 m | - | 18.8; 24.3; 27.5 | 197 |
| **IV** | violet | 40 | 2.5 | 995 m | 1510 m | - | 18.4; 24.0; 30.0 | 204 |
| **V** | red | 25 | 4.4 | 990 m | 1510 m | ν(C-S): 840 m<br>ν(C≡N): 2080 m | 20.5; 30.0 | 190 |
| **VI** | red | 54 | 11.3 | 1000 m | 1500 m | - | 19,5; 25.0; 30.5 | 156 |
| **VII** | red | 65 | 9.2 | 1000 m | 1500 m | - | 19.4; 25.0; 30.0 | 160 |
| **VIII** | orange | 32 | 10.4 | 1000 m | 1500 m | ν(C-S): 840 m<br>ν(C≡N): 2090 s | 21.5; 25.6; 28.8 | 74 |
| **IX** | red | 27 | 132.4 | 995 m | 1500 m | $\nu_3(ClO_4)$: 1090 s<br>$\nu_4(ClO_4)$: 620 m | 19.5; 31.2 | - |
| **X** | red | 16 | 98.0 | 995 m | 1510 m | $\nu(PF_6)$: 840 s | 20.0; 30.4 | 220 |
| **XI** | violet | 65 | 1.8[b] | 990 m | 1520 w | - | 19.5; 31.2; 36.1 | 66 |
| **XII** | pink | 64 | 2.1[b] | 1010 w | 1510 m | - | 19.2; 30.3; 35.0 | 72 |
| **XIII** | orange | 61 | 2.6[b] | 1000 w | 1510 vs | ν(C-S): 840 w<br>ν(C≡N): 2100 vs | 21.2; 30.0; 36.9 | 85 |

[a] In acetone solution, $[Ni^{2+}] = 10^{-3}$ mol.dm$^{-3}$
[b] In nitromethane solution, $[Ni^{2+}] = 10^{-3}$ mol.dm$^{-3}$
[c] In nujol
$T_t$ Melting point

## References


1. Maxfield P. L.: *Inorg. Nucl. Chem. Lett.* **6**, 693 (1970).
2. McCleverty J. A. and Morrison N. J.: *J. Chem. Soc., Dalton Trans.*, 1976, 541.
3. Fackler J. P., Lin I. J. B. and Andrews J.: *Inorg. Chem.* **16**, 450 (1977).
4. Chan L. T., Chen H. W., Fackler J. P., Masters A. F. and Pan W. H.: *Inorg. Chem.* **21**, 4291 (1982).
5. Ramalingam K., Aravamudan G., Seshasayee M. and Subramanyan Ch.: *Acta Crystallogr.* **C40**, 965 (1984).
6. Ramalingam K., Aravamudan G. and Seshasayee M.: *Inorg. Chim. Acta* **128**, 231 (1987).
7. Pastorek R., Kameníček J., Březina F., Lasovský J., Šindelář Z. and Ondráček J.: *Acta Univ. Palacki. Olom. Chemica* **32**, 7 (1993).
8. Pastorek R., Kameníček J., Březina F., Šindelář Z., Jehlářová E., Duffy N. V. and Glowiak T.: *Chem. Papers* **48**, 317 (1994).
9. Venkatachalam V., Ramalingam K., Mak T. C. W. and Bao-Sheng L.: *Polyhedron* **15**, 1295 (1996).
10. Venkatachalam V., Ramalingam K., Bocelli G. and Cantoni A.: *Inorg. Chim. Acta* **257**, 49 (1997).
11. Pastorek R., Kameníček J., Cvek B., Pavlíček M., Šindelář Z. and Žák Z.: *J. Coord. Chem.* **56**, 1123 (2003).
12. Kameníček J., Pastorek R., Cvek B. and Taraba J.: *Z. Kristallogr. NCS* **218**, 205 (2003).
13. Prakasam B. A., Ramalingam K., Bocelli G. and Olla R.: *Z. Anorg. Allg. Chem.* **630**, 301 (2004).
14. Prakasam B. A., Ramalingam K., Saravanan M., Bocelli G. and Cantoni A.: *Polyhedron* **23**, 77 (2004).
15. Husárek J., Pastorek R., Maloň M., Šindelář Z. and Pavlíček M.: *J. Serb. Chem. Soc.* (in press, the references therein).
16. Husárek J. and co-authors: Synthesis and structural characterization of the Ni(II) benzylbutyldithiocarbamate complexes with triphenylphosphine in the coordination sphere (unpublished results).
17. Přibil R.: Komplexometrické titrace, SNTL, Praha 1955, p. 22.
18. Jureček M.: Organická analýza II, ČSAV, Praha 1957, p. 140.
19. Gmelins Handbuch der Anorganischen Chemie, Nickel, Teil C, Lief. 2, Verlag Chemie, GmbH, Weinheim 1969, p. 996.
20. Gmelins Handbuch der Anorganischen Chemie, Nickel, Teil C, Lief. 2, Verlag Chemie, GmbH, Weinheim 1969, p. 997.
21. Geary W. J.: *Coord. Chem. Rev.* **7**, 81 (1971).
22. Scholer R. P. and Merbach E. A.: *Inorg. Chim. Acta* **15**, 15 (1975).
23. Ballester L., Gutierrez A., Perpinan M. F. and Ruiz-Valero: *Polyhedron* **15**, 1103 (1996).
24. Černikova I. E., Chartonik I. A., Umrejko D. S., Kavrikov A. B. and Afanov V. I.: *Koord. Chim.* **15**, 1695 (1989).
25. Tsipis C. A., Kessissoglou D. P. and Katsoulos G. A.: *Chim. Chron*, *New Series* **14**, 195 (1985).
26. Larionov S. V., Patrina L. A., Oglezneva I. M. and Uskov E. M.: *Koord. Chim.* **10**, 92 (1984).
27. Lever A. B. P.: Inorganic Electronic Spectroscopy (Elsevier, Amsterdam, 1984), p. 534.
28. Tsipis C. A., Kessissoglou D. P. and Manoussakis G. E.: *Inorg Chim. Acta* **65**, L137 (1982).
29. Tsipis C. A., Meleziadis I. J., Kessissoglou D. P. and Katsoulos G. A.: *Inorg. Chim. Acta* **90**, L19 (1984).



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# OXO DERIVATIVES OF QUINOXALINE VIII. THE STUDY OF THE CONFORMATION OF SOME POLYCYCLIC N-H ACIDS WITH QUINOXALINE AND [1,2,4]TRIAZINE CYCLES[1]

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## Abstract

Following some previous communications[2-4] we foccused our attention to the synthesis of some compounds containing 6-azauracil and quinoxaline cycles. We also concentrated on theoretical considerations about their possible conformations.

A general formula is presented for the calculation of mutual distances of arbitrary atoms in any planar molecules.

**Key Words:** *limit planar conformation, 3-substituted 1,2-dihydro-quinoxaline-2-one, 1-aryl-6-azauraciles, mutual distances of N-H groups calculations*

## Introduction

Non-condensed polynuclear compounds with acidic N-H groups can exhibit due to free rotation various conformations, which differ in mutual distances of the acidic NH groups. They should be able to interact with biomolecules by means of intermolecular hydrogen bonds on two remote bonding centres and can affect their spatial arrangement.

In the past years we have paid attention to two[5-9] and three-ring[3,9] compounds where the role of heterocycles with acidic N-H groups was played by 6-azauracil cycles.

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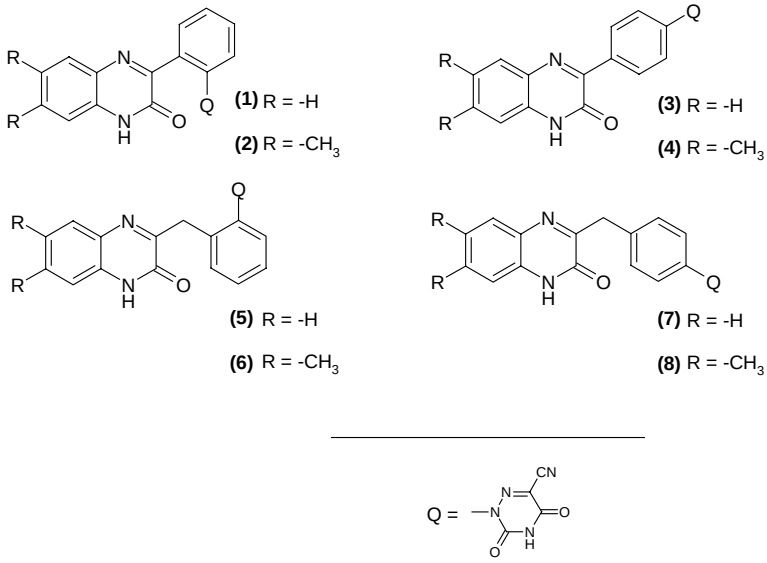
The subject of this communication is the extention of this area for compounds which besides 6-azauracil cycle contain the 2-oxo-1,2-dihydro-quinoxaline cycle of somewhat different N-H groups as compared with the 6-azauracil ring. We have focused on the study of compounds where the 2-oxo-1,2-dihydro-quinoxaline cycle is connected in position 3 with 6-azauracil cycle by either phenyl or benzyl groups and on their limit planar conformations. (Scheme 1).

Compounds of this type seem to be very interesting from the point of view of their possible conformations and the ability to form intermolecular hydrogen bonds with substrates at two bonding centres.

## Results and Discussion

Scheme 1.




The way how to evaluate the possible conformations of polyatomic molecules with free rotating cycles can be illustrated at compounds (**1-8**).

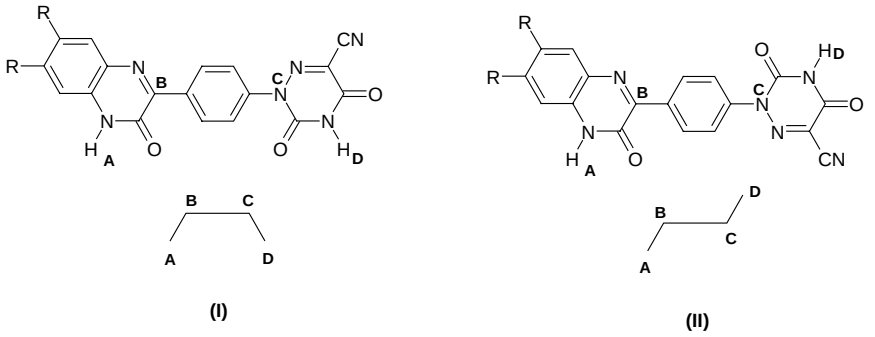
Due to free rotation all cycles of tricyclic compounds (**1-8**) occupy the various spatial conformations. These conformations influence not only the whole form of molecules but also the mutual distances of bonding centres such as for example N-H group of 6-azauracil and 1,2-dihydroquinoxaline-2-one cycles which can play the important role in interactions of these compounds with biomolecules together at two binding centres.

The simplified scheme of all possible spatial conformations of mentioned compounds offers only conformations which are planar.

Their number is given by the number of combinations of possible mutual positions of axis of rotation in the plane. Instead of the whole formulas we can use the bent line where the individual line segments (abscissa) represent the mentioned axis of rotation and the initial and final abscissa illustrates the connecting line of an atom by means of which the cycle is connected with a substituent on a cycle for which we are interested.

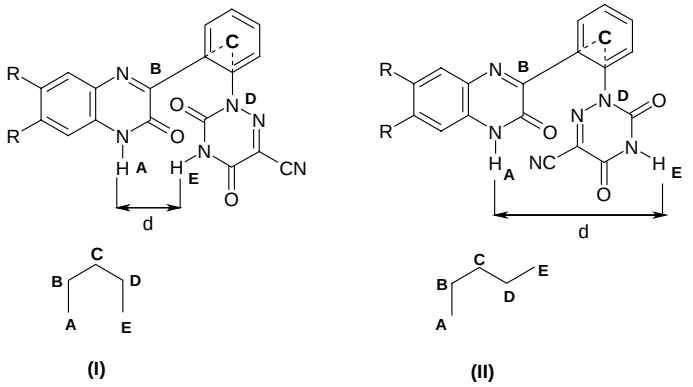
In the case of **3** and **4** compounds having only one axis of rotation (**BC**) exist only two different planar conformations.

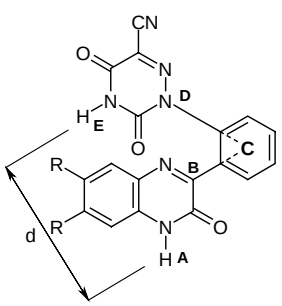
Scheme 2. The planar conformatins of compounds **3** resp. **4**.

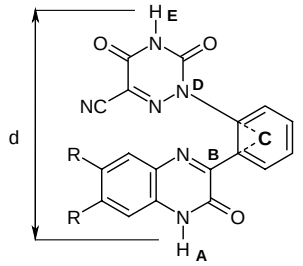


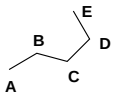

In the case of compounds **1** and **2** with the axis of rotation BC and CD are 4 different planar conformations where the formula is presented only at the first conformation (point C is an intersection of axis of rotation).

Scheme 3. The planar conformatins of compounds **1** resp. **2**.

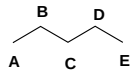




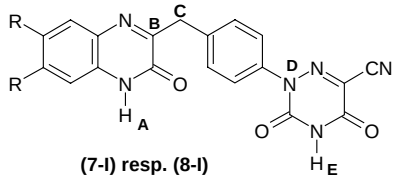

(III)




(IV)

Quite analogical case can be seen with compounds **7** and **8** where also 4 limit planar conformations are possible. We present for example only formula of conformation **7-I** resp. **8-I**.

Scheme 3. The planar conformatins of compounds **7** resp. **8**.

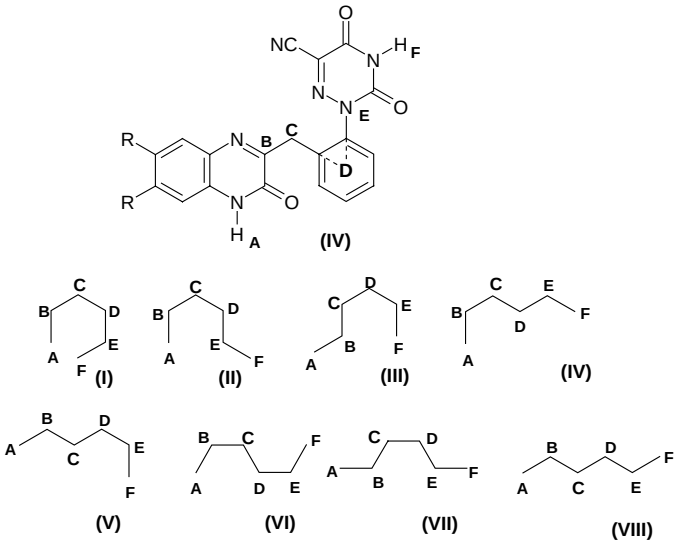



**(7-I) resp. (8-I)**

The compounds **5** and **6** have the eight possible planar conformations (**I-VIII**). We present for example only formula of conformation **5-IV** resp. **6-IV**.

If we know all lengthes of mentioned bindings resp. axis and all angles we can calculate[10] the mutual distance of arbitrary bonding centres, e.g. acidic hydrogens of N-H groups with all planar conformations. In this case with respect to these distances with compounds **1, 2, 7** and **8** we can see equivalent conformations **II** and **III** and with compounds **5** and **6** we can see equivalent conformations **II**, **III** and **IV**, **V**. For the compound **1** resp. **2** are e.g. the calculated values for conformers **I-IV** as follows: **I**- d=1,63Å, **II-III** d=5,69Å, **IV**- d=8,97Å.

The presented planar conformations provide only simplified representation of spatial possibilities of the mentioned molecules. The real conformation depends on many factors, e.g. the influence of solvents and the interactions between molecules in crystal lattice.




Certain information about the conformation can be given by the calculation of the molecule without outer influences of a solvent or other molecules in a crystal lattice. This can be illustrated at the compound **1**[2]. The real spatial conformation of this compound was calculated by following way. Initial study of conformers of compound **1** was carried out with the AM1 semi-empirical method, followed by ab-initio calculations. A potential energy surface (PES) scan was performed using HyperChem 5.01 with HyperSpin 2.0 software and the AM1 method with Polak-Ribiere optimization algoritmus was employed. Four selected conformers (Figure 1) were then minimized using Hartree-Fock (HF) method with SDDALL[11-15] effective core potential basis set under tight optimization conditions. Vibrational frequencies and thermochemical data were obtained at the same level of theory. All these analyses were performed using Gaussian 98 for Windows software.

The flexible PES scan results were analyzed in Statistica 6.0 software, surface was fitted to the data with the least square method.

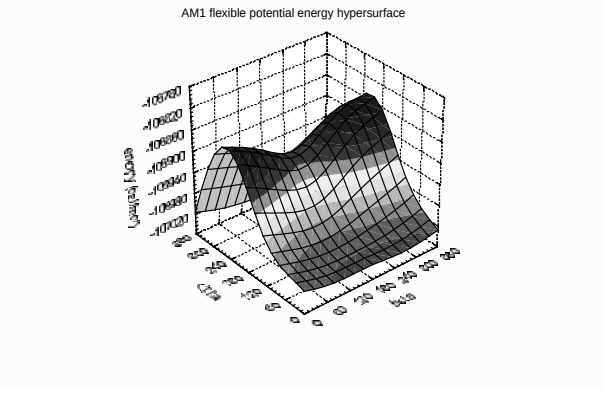



**Figure 1**: Plot of potential energy (AM1) against torsion angles α and β of compound **1**

Figure (AM 1 flexible potential energy hypersurface) shows a plot of the potential energy of **1** versus the two torsion angles α and β. The most stable conformer (α = 41°, β = –103°) is positioned in a wide valley.

Table 1. shows important torsion angles, space distances of hydrogen atoms, and total energy of conformers. The global minimum found by ab-initio method does not significantly differ from semiempirical global minimum in the two mentioned torsion angles. The nonsignifficant energy differences among conformers indicate that all could be easy under normal temperature accessible and thus the two monitored dihedrals are free except prohibited region.

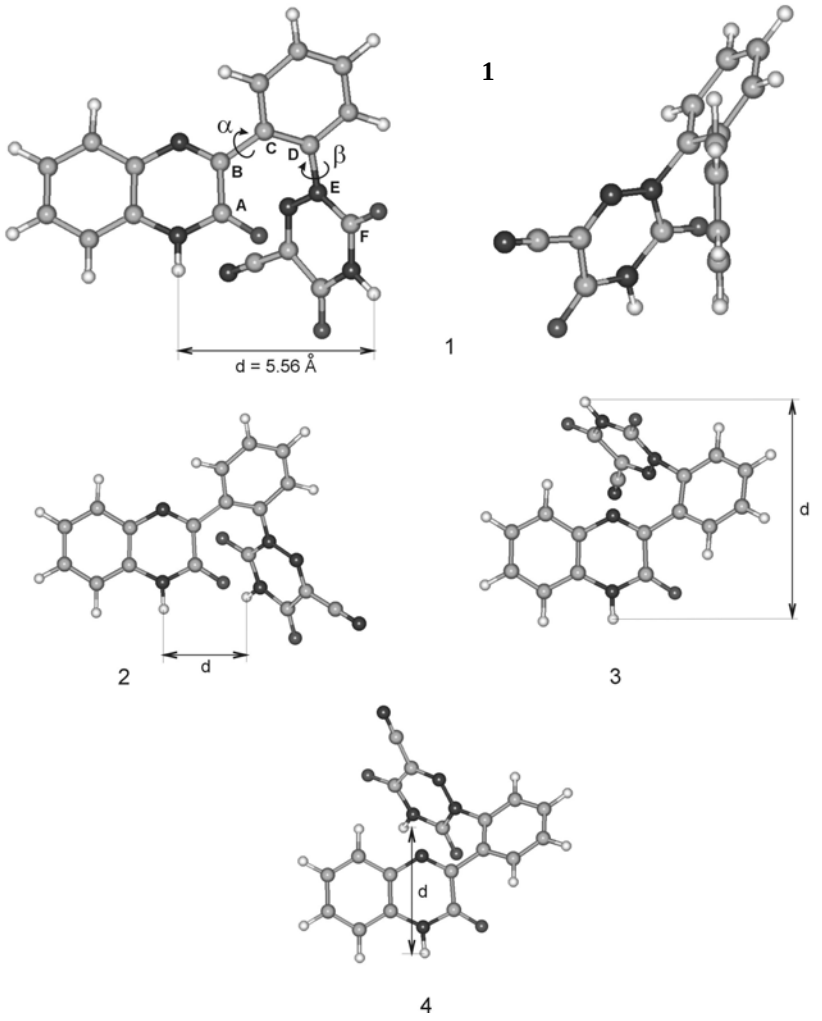


Table 1: Torsion angles and energy diffrences of four optimized conformers of compound **1**

| conformer | α(A-B-C-D) | β(C-D-E-F) | bold H-H (Å) | SCF energie (Hart) | $\Delta E^a$ (kcal/mol) |
|---|---|---|---|---|---|
| 1 | 44,8 | -115,6 | 5,56 | -210,1274645 | 0,0000 |
| 2 | 39,6 | 54,6 | 4,87 | -210,1260488 | 0,8883 |
| 3 | -36,8 | 101,3 | 7,82 | -210,1259178 | 0,9706 |
| 4 | -38,4 | -67,1 | 6,44 | -210,1254443 | 1,2677 |

[a] energy difference between global minimum and other conformers

In the case of other polynuclear compounds it would be quite analogous. In the case of polyatomic hydrazones **1-8,** however, we should take into consideration hydrazone double bonds without free rotation.


## Acknowledgments

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## Reference


1. Part 6 of „Polycyclic Heterocycles with Acidic N-H Group“ series. For previous paper see ref. 4.
2. Wiedermannová I., Slouka J.: *J. Heterocyclic Chem.*, **38**, 1465 (2001).
3. Bílek P., Slouka J.: *J. Heterocyclic Chem*., **39**, 357 (2002).
4. Wiedermannová I., Otyepka M., Stýskala J., Slouka J.: *Arkivoc*, **XV**, 65 (2003).
5. Slouka J.. *Pharmazie* **34**, 796 (1979); **35**, 794 (1980).
6. Slouka J.: *Coll. Czech. Chem. Commun.* **44**, 2938 (1979); **55**, 2967 (1990).
7. Slouka J., Bekárek V., Hlaváč: J. *Coll. Czech. Chem. Commun.* **59**, 2741 (1994).
8. Hlaváč J., Slouka J.: *J. Heterocyclic Chem.* **34**, 917 (1997).
9. Hlaváč J., Slouka J., Hradil P., Lemr K.: *J. Heterocyclic Chem.* **37**, 115 (2000).
10. Slouka J.: *Coll. Czech. Chem. Commun*. **55**, 2967 (1990).
11. Dewar M., Thiel W.: *J. Am. Chem. Soc*. **99**, 4499 (1977).
12. Dewar M., McKee M., Rzepa H.: *J. Am. Chem. Soc.* **100**, 3607 (1978).
13. Choi D.S., Chong Y.S., Whitehcad D. and Shimizu K.D.: *Org. Lett.* **3**, 3757 (2001).
14. Gardner R.R., McKay S.L., Gellman S.H.: *Org. Lett.* **2**, 2335 (2000).
15. Fuentealba P., Preuss H., Stoll H., Szentpaly L. V.: *Chem. Phys. Lett*. **89**, 418 (1989).



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# BINUCLEAR NICKEL(II) DITHIOCARBAMATE COMPLEXES WITH SELECTED AROMATIC MONOTHIOLS AS BRIDGING LIGANDS

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**Abstract**

The work reports on the synthesis and physico-chemical study of binuclear Ni(II) dithiocarbamate compounds of the composition $[Ni(\mu\text{-}SR')(Rdtc)]_2$ (HSR' = benzenethiol, 4-methylbenzenethiol, 2-naphthalenethiol; Rdtc = benzylisopropyl-, benzylbutyl-, cyclohexylethyl-, dipentyl-, dibenzyldithiocarbamate). All the synthesized coordination compounds have been characterized by means of elemental analysis, complexometric titrations with chelatone 3, IR and UV/VIS spectroscopy, thermal analysis, magnetochemical and conductivity measurements. These methods have shown that coordination compounds are diamagnetic, non-electrolytes, with two square-planar $NiS_4$ chromophores.

**Key words:** *Nickel(II) dithiocarbamate complexes; aromatic monothiols; synthesis; physico-chemical study.*

## Introduction

The wide attention is paid to study of the dithiocarbamate compounds at present, not only for their interesting coordination behaviour but also for their potential

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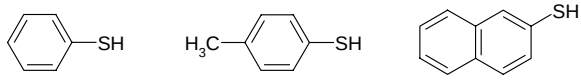
use in applied investigation[1-3]. For example, they are used in agriculture as fungicides and pesticides. In view of this work we have searched for information on binuclear Ni(II) dithiocarbamate complexes with monothiols in the literature, where the monothiols coordinate *via* sulfur atom and they create bridges between the two nickel atoms. We have found several articles[4-9], in which the authors have focused on synthesis and physico-chemical study Ni(II) coordination compounds of the general type $[Ni(\mu\text{-}SR')(Rdtc)]_2$. For example, McCleverty *et al.*[4] and Darkwa *et al.*[5,6] have studied Ni(II) compounds $[Ni(\mu\text{-}SR')(Rdtc)]_2$ (HSR' = methanethiol, 2-propanethiol, 2-methyl-2-propanethiol, α-toluenethiol, benzenethiol, 4-methylbenzenethiol, ethanethiol, 4-chlorobenzenethiol, 4-chlorobenzenemethanethiol; Rdtc = dibutyl-, dimethyl-, diethyldithiocarbamate). Schulbert *et al.*[7] has prepared and structurally characterized the complex $[Ni(\mu\text{-}Sme)(Hmedtc)]_2$ (me = methyl). It is notable that similar compounds have been also isolated and characterized in our department. In our previous works[8,9] we have systematically studied Ni(II) dithiocarbamate complexes of the composition $[Ni(\mu\text{-}SR')(Rdtc)]_2$ (HSR' = benzenethiol, 4-methylbenzenethiol, 2-naphthalenethiol, thiosalicylic acid, 1-hexanethiol, 1-butanethiol; Rdtc = morpholine-, piperidine-, pyrrolidine-, 4-aminoantipyrine-, hexamethyleneiminedithiocarbamate). The results of physico-chemical study have shown that all these coordination compounds are diamagnetic, non-electrolytes, with binuclear arrangement of coordination sphere (two square-planar $NiS_4$ chromophores).

In this paper we are reporting on synthesis and physico-chemical study of new Ni(II) coordination compounds containing the symmetrical or non-symmetrical dithiocarbamate ligand and aromatic monothiol (Fig. 1) in the coordination sphere of two nickel atoms.




a) b) c)

**Fig. 1.** The used aromatic monothiols and their structural formulae {**a)** benzenethiol ($C_6H_5SH$), **b)** 4-methylbenzenethiol ($C_7H_7SH$), **c)** 2-naphthalenethiol ($C_{10}H_7SH$)}

## Materials and methods

All chemicals purchased from commercial sources were of high purity. Benzenethiol (97 %), 4-methylbenzenethiol (98 %), 2-naphthalenethiol (97 %), N-cyclohexylethylamine (98 %), N-benzylbutylamine (98 %), dibenzylamine (97 %) were obtained from Aldrich Co.; dipentylamine (97 %) was product of Fluka Co.; N-benzylisopropylamine (97 %) was procured from Lancaster Co. and triethylamine was purchased from Downs Development Chemicals Limited. The other reagents were supplied by Lachema Co. and all were of p.a. purity. The starting compounds $[NiX(Rdtc)(PPh_3)]$ (X = Cl or Br) were synthesized according to the procedures described in the literature[10-14].

The content of nickel was determined by chelatometric titration on murexide as an indicator[15] after dissolving of sample in $HNO_3$. The elemental analyses (C, H, N, S) were performed on an EA 1108 instrument (Fisons). The room temperature magnetic susceptibilities of all compounds were measured using Faraday's method with $Co[Hg(NCS)_4]$ as a calibrant on a laboratory designed instrument with a Sartorius 4434 MP-8 microbalance. The molar conductivities of $10^{-3}$ M acetone solutions of all complexes were measured with a Conductivity Hand-Held Meter LF 330 (WTW GmbH) at 25 ºC. Diffuse-reflectance electronic absorption spectra (45000–11000 $cm^{-1}$) were carried out on a Specord M 40 and IR spectra (4000–400 $cm^{-1}$) were recorded on a Specord M 80 (Carl Zeiss, Jena) using nujol mulls. The thermal analysis was performed on an Exstar 6000, TG/DTA 6200 device (Seiko, Japan; sample weight 5.9–11.3 mg, temperature range 20–1000 °C, gradient 5.0 ºC/min; an air atmosphere). The melting points were determined by means of Boëtius apparatus (VEB Wägetechnic Rapido, PHMK 79/2122).

## Syntheses of the complexes

$[Ni(\mu\text{-}SR')(Rdtc)]_2$ (**I**–**VIII**, see Table 1)

To a solution of $[NiCl(Rdtc)(PPh_3)]$ (Rdtc = benzylisopropyl-, benzylbutyl- or cyclohexylethyldithiocarbamate) (1 mmol) in chloroform (10 $cm^3$) aromatic monothiol (1 mmol) was added. The reaction mixture was stirred at room temperature for *ca.* 5 min. and filtered. Triethylamine (1 mmol) was then added, dropwise with stirring, to the violet filtrate. The solution turned green immediately and it was left to evaporate at room temperature. After a few days the solid evaporation residue was obtained, which was several times decanted with ethanol for complexes **I**–**III**, petroleum ether for **IV**–**VI**, **VIII** or methanol for **VII**. The green product was filtered off, washed with n-hexane for **I**–**III**, petroleum ether for **IV**–**VIII** and dried under an IR lamp at 40 °C. The complexes **I**–**IV** and **VI** were moreover purified by recrystallization in dichloromethane.

$[Ni(\mu\text{-}SR')(Rdtc)]_2$ (**IX**–**XII**, see Table 1)

These complexes were prepared by the same procedure, but starting compound $[NiBr(Rdtc)(PPh_3)]$ (Rdtc = dipentyl- or dibenzyldithiocarbamate) (1 mmol) was used. In all cases an oily product was obtained, which was transformed into a powdered substance after the addition of methanol. The final green product was then filtered off, washed with methanol and dried under an IR lamp at 40 °C.

## Results and discussion

The green Ni(II) complexes were synthesized in moderate yields by the reaction $[NiX(Rdtc)(PPh_3)]$ with aromatic monothiol and triethylamine in chloroform according to the following general scheme:

$$[NiX(Rdtc)(PPh_3)] + HSR` + Et_3N \longrightarrow 1/2\ [Ni(\mu\text{-}SR`)(Rdtc)]_2 + PPh_3 + [Et_3NH]X$$

where X = Cl or Br, HSR' = benzenethiol, 4-methylbenzenethiol, 2-naphthalenethiol and Rdtc = benzylisopropyl-, benzylbutyl-, cyclohexylethyl-, dipentyl- or dibenzyldithiocarbamate.

The isolated coordination compounds are stable on air; they are soluble in chloroform, dichloromethane, acetone and insoluble in n-hexane, petroleum ether, ethanol, methanol and water. The composition and elemental analyses of the new Ni(II) complexes are given in Table 1; yields, molar conductivities, spectral data, melting points (M.p.) and results of the thermal analysis are summarized in Table 2.

All compounds are diamagnetic. The values of the molar conductivities (0.1–6.5 $S.cm^2.mol^{-1}$) clearly showed their non-ionic nature in acetone solution[16]. The results of the magnetochemical and conductivity measurements allow us to assume a square-planar coordination around Ni(II) atoms. IR and UV/VIS spectroscopy also supported this conclusion. IR spectra of isolated compounds were not studied in detail. The bands were monitored only, which appertain to vibrations characteristic for dithiocarbamate ligand and aromatic monothiol. In IR spectrum of all complexes the maxima were observed in the region 1500–1525 $cm^{-1}$ and 990–1010 $cm^{-1}$. These maxima are typical for dithiocarbamates and can be attributed to ν(C···N) and ν(C···S) vibrations, respectively[17,18]. The maximum of the ν(C–S) vibration[19] was also found in the interval 730–742 $cm^{-1}$, which suggestive of presence of the aromatic monothiol in our coordination compounds. Diffuse-reflectance electronic spectra exhibited the absorption maxima in the region 15000–16000 $cm^{-1}$ and 21300–25600 $cm^{-1}$. All these maxima are characteristic for square-planar Ni(II) complexes and may be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions, respectively[20,21]. The intensive maxima between 28500–36200 $cm^{-1}$ are probably connected with the intraligand transitions in the $S_2CN^-$ group[17].

Thermal analysis was applied to all prepared compounds. The thermal decomposition of the complexes **I**–**VIII** containing non-symmetrical dithiocarbamate ligands started in the temperature interval 86–160 °C while the beginning of the decomposition for complexes **IX**–**XII** with symmetrical dithiocarbamate ligands was between 192–229 °C. It follows that the coordination compounds **IX**–**XII** are thermally more stable. In the case of complexes **II**, **V**, **IX** and **X** endo-effect was observed in the interval 103–161 °C on the DTA-curves, which was not accompanied by a mass loss on the TG-curves. The endo-effects are probably connected with the melting process. This affirmation was satisfactorily confirmed by melting points determined on a Boëtius apparatus (Table 2). The exo-effects were also identified in the temperature interval 219–561 °C on the DTA-curves, which are probably caused by a total destruction of the organic parts in the studied complexes. The destruction influences course of the thermal decomposition significantly and induces mass changes on the TG-curves. In general terms, the course of the thermal decomposition of all compounds is very similar. We depict thermal analysis of $[Ni(\mu\text{-}SC_6H_5)(pe_2dtc)]_2$ (**IX**) for illustration in Fig. 2.

We were not able to prepare a single crystal suitable for X-ray structural analysis, which could unambiguously confirm all experimental results as well as our general idea about the structure of the studied compounds. However, on the basis of X-ray structural analysis of the similar complex $[Ni(\mu\text{-}Sme)(Hmedtc)]_2$ (me = methyl)[7] we

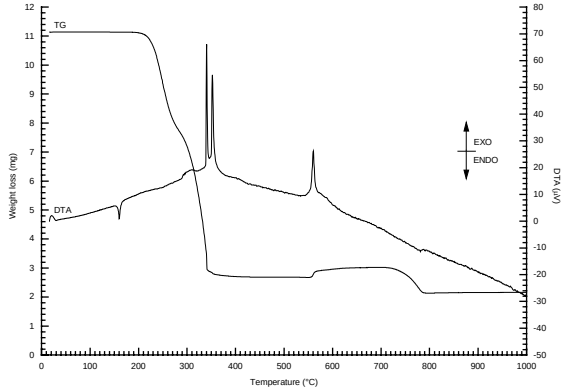



**Fig. 2.** Thermal analysis of $[Ni(\mu\text{-}SC_6H_5)(pe_2dtc)]_2$ (**IX**)

assume that we have synthesized binuclear Ni(II) coordination compounds, in which the monothiols coordinate *via* sulfur atom and they create bridges between the two nickel atoms (two square-planar $NiS_4$ chromophores, Fig. 3).

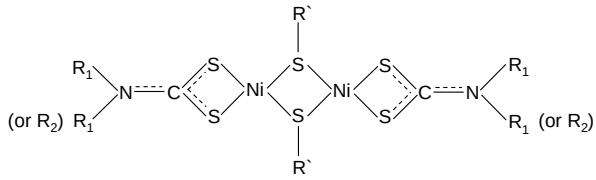



**Fig. 3.** The predicted square-planar arrangement of the $NiS_4$ chromophores for binuclear Ni(II) complexes **I**–**XII** ($R_1R_2dtc$ = non-symmetrical dithiocarbamate ligand, dtc = $S_2CN^-$)

**Table 1.** Chemical composition, molecular weight and elemental analyses of the complexes

| Complex | | M.W. | Found/Calcd. [%] | | | | |
|---|---|---|---|---|---|---|---|
| | | | Ni | C | H | N | S |
| **I** | $[Ni(\mu\text{-}SC_6H_5)(bz^iprdtc)]_2$ $C_{34}H_{38}N_2Ni_2S_6$ | 784.47 | 14.9/15.0 | 51.7/52.1 | 4.5/4.9 | 3.6/3.6 | 24.1/24.5 |
| **II** | $[Ni(\mu\text{-}SC_7H_7)(bz^iprdtc)]_2$ $C_{36}H_{42}N_2Ni_2S_6$ | 812.52 | 14.2/14.5 | 52.8/53.2 | 5.5/5.2 | 3.9/3.5 | 23.1/23.7 |
| **III** | $[Ni(\mu\text{-}SC_{10}H_7)(bz^iprdtc)]_2$ $C_{42}H_{42}N_2Ni_2S_6$ | 884.59 | 13.4/13.3 | 56.6/57.0 | 5.2/4.8 | 3.3/3.2 | 21.0/21.8 |
| **IV** | $[Ni(\mu\text{-}SC_6H_5)(bzbudtc)]_2$ $C_{36}H_{42}N_2Ni_2S_6$ | 812.52 | 14.1/14.5 | 52.8/53.2 | 5.2/5.2 | 3.8/3.5 | 24.2/23.7 |
| **V** | $[Ni(\mu\text{-}SC_7H_7)(bzbudtc)]_2$ $C_{38}H_{46}N_2Ni_2S_6$ | 840.58 | 14.1/14.0 | 54.1/54.3 | 6.0/5.5 | 3.3/3.3 | 23.2/22.9 |
| **VI** | $[Ni(\mu\text{-}SC_{10}H_7)(bzbudtc)]_2$ $C_{44}H_{46}N_2Ni_2S_6$ | 912.64 | 12.4/12.9 | 57.4/57.9 | 5.4/5.1 | 3.4/3.1 | 21.4/21.1 |
| **VII** | $[Ni(\mu\text{-}SC_7H_7)(cetdtc)]_2$ $C_{32}H_{46}N_2Ni_2S_6$ | 768.51 | 14.9/15.3 | 50.7/50.0 | 6.5/6.0 | 3.5/3.7 | 24.5/25.0 |
| **VIII** | $[Ni(\mu\text{-}SC_{10}H_7)(cetdtc)]_2$ $C_{38}H_{46}N_2Ni_2S_6$ | 840.58 | 13.7/14.0 | 54.9/54.3 | 5.9/5.5 | 3.0/3.3 | 23.1/22.9 |
| **IX** | $[Ni(\mu\text{-}SC_6H_5)(pe_2dtc)]_2$ $C_{34}H_{54}N_2Ni_2S_6$ | 800.60 | 14.9/14.7 | 51.4/51.0 | 6.9/6.8 | 3.5/3.5 | 23.1/24.0 |
| **X** | $[Ni(\mu\text{-}SC_7H_7)(pe_2dtc)]_2$ $C_{36}H_{58}N_2Ni_2S_6$ | 828.65 | 14.0/14.2 | 52.2/52.2 | 7.0/7.1 | 3.4/3.4 | 23.0/23.2 |
| **XI** | $[Ni(\mu\text{-}SC_{10}H_7)(pe_2dtc)]_2$ $C_{42}H_{58}N_2Ni_2S_6$ | 900.71 | 12.9/13.0 | 56.8/56.0 | 6.3/6.5 | 2.9/3.1 | 21.5/21.4 |
| **XII** | $[Ni(\mu\text{-}SC_7H_7)(bz_2dtc)]_2$ $C_{44}H_{42}N_2Ni_2S_6$ | 908.61 | 12.3/12.9 | 58.0/58.2 | 4.2/4.7 | 3.1/3.1 | 20.5/21.2 |

$bz^i$prdtc = benzylisopropyldithiocarbamate, bzbudtc = benzylbutyldithiocarbamate, cetdtc = cyclohexylethyldithiocarbamate, $pe_2$dtc = dipentyldithiocarbamate, $bz_2$dtc = dibenzyldithiocarbamate.

**Table 2.** The physico-chemical properties of the complexes

| Complex | | Yield [%] | $\lambda_M$[a] [S.cm$^2$. mol$^{-1}$] | UV/VIS[b] [×10$^3$ cm$^{-1}$] | IR [cm$^{-1}$][b] ν(C=S) | ν(C=N) | ν(C–S) | TA [°C] $T_d$ | $T_{en}$ | M.p. [°C] |
|---|---|---|---|---|---|---|---|---|---|---|
| **I** | [Ni(μ-$SC_6H_5$)($bz^iprdtc$)]$_2$ | 26 | 0.5 | 15.8; 21.8; 28.8; 35.6 | 990w | 1512w | 740s | 140 | – | 116 |
| **II** | [Ni(μ-$SC_7H_7$)($bz^iprdtc$)]$_2$ | 27 | 6.5 | 15.9; 21.8; 28.5; 35.3 | 992w | 1512m | 735w | 160 | 124 | 124 |
| **III** | [Ni(μ-$SC_{10}H_7$)($bz^iprdtc$)]$_2$ | 18 | 0.2 | 15.6; 21.5; 28.8; 35.8 | 995w | 1510w | 738w | 106 | – | 102 |
| **IV** | [Ni(μ-$SC_6H_5$)(bzbudtc)]$_2$ | 23 | 6.5 | 15.8; 22.6; 24.8; 29.4 | 1005m | 1525w | 742s | 98 | – | 192[c] |
| **V** | [Ni(μ-$SC_7H_7$)(bzbudtc)]$_2$ | 18 | 2.2 | 15.7; 22.0; 24.9; 29.2 | 1005m | 1521w | 740m | 122 | 103 | 101 |
| **VI** | [Ni(μ-$SC_{10}H_7$)(bzbudtc)]$_2$ | 19 | 3.3 | 15.2; 22.7; 24.8; 30.0 | 1010m | 1522w | 730m | 115 | – | 241[c] |
| **VII** | [Ni(μ-$SC_7H_7$)(cetdtc)]$_2$ | 15 | 4.5 | 16.0; 21.6; 24.9; 35.4 | 1001w | 1514w | 735s | 86 | – | 104[c] |
| **VIII** | [Ni(μ-$SC_{10}H_7$)(cetdtc)]$_2$ | 16 | 4.4 | 15.0; 21.3; 25.1; 29.7 | 1008s | 1522m | 732s | 103 | – | 84 |
| **IX** | [Ni(μ-$SC_6H_5$)($pe_2$dtc)]$_2$ | 36 | 1.2 | 15.6; 21.6; 25.0; 36.0 | 998m | 1500m | 740m | 197 | 161 | 160 |
| **X** | [Ni(μ-$SC_7H_7$)($pe_2$dtc)]$_2$ | 31 | 0.4 | 15.6; 21.6; 25.0; 36.2 | 1010m | 1500s | 730w | 206 | 154 | 153 |
| **XI** | [Ni(μ-$SC_{10}H_7$)($pe_2$dtc)]$_2$ | 35 | 0.2 | 15.4; 21.5; 25.6; 35.0 | 995w | 1500s | 738w | 229 | – | 201 |
| **XII** | [Ni(μ-$SC_7H_7$)($bz_2$dtc)]$_2$ | 31 | 0.1 | 15.8; 21.7; 24.2; 34.5 | 998m | 1510m | 742m | 192 | – | 187 |

[a] Measured in acetone solution, $[Ni^{2+}] = 10^{-3}$ mol.dm$^{-3}$.
[b] Measured in nujol.
$T_d$ – beginning of the thermal decomposition.
$T_{en}$ – endo-effect.
M.p.– melting point, [c] Complex melts with decomposition.

## References


1. Tiexeira M., Moura I., Xavier A. V., DerVartanian D. V., LeGall J., Peck, Jr. H. D., Huynh B. H. and Moura J. J. G.: *Eur. J. Biochem.* **130**, 481 (1983).
2. Hersh E. M., Brewton G., Abrams D., Barlett J., Galpin J., Gill P., Gorter R., Gottlieb M., Jonikas J. J., Landesman S., Levine A., Marcel A., Petersen E. A., Whiteside M., Zahradnik J., Negron C., Boutitie F., Caraux J., Dupuy J. M. and Salmi L. R.: *J. Am. Med. Assoc.* **265**, 1538 (1991).
3. Montgomery J. H.: Agrochemical Desk Reference Environmental Data, Lewis Publishers, Michigan 1993, p. 261.
4. McCleverty J. A. and Morrison N. J.: *J. Chem. Soc., Dalton Trans.* **1976**, 541.
5. Darkwa J., Koczon L. M. and Rost J. M.: *Synth. React. Inorg. Met.-Org. Chem.* **23**, 509 (1993).
6. Darkwa J., Osei-Twum E. Y. and Litorja, Jr. L. A.: *Polyhedron* **18**, 1115 (1999).
7. Schulbert K. and Mattes R.: *Z. Naturforsch.* **49b**, 770 (1994).
8. Pastorek R., Trávníček Z., Šindelář Z. and Březina F.: *Transition Met. Chem.* **24**, 304 (1999).
9. Pavlíček M., Pastorek R. and Šindelář Z.: *Acta Univ. Palacki. Olom., Chemica* **41**, 43 (2002).
10. Pastorek R., Kameníček J., Trávníček Z., Husárek J. and Duffy N. V.: *Polyhedron* **18**, 2879 (1999).
11. Pastorek R., Kameníček J., Cvek B., Pavlíček M., Šindelář Z. and Žák Z.: *J. Coord. Chem.* **56**, 1123 (2003).
12. Husárek J., Pastorek R., Maloň M., Šindelář Z. and Pavlíček M.: *J. Serb. Chem. Soc.* (in press).
13. Cvek B., Husárek J., Pastorek R., Maloň M., Šindelář Z. and Pavlíček M.: Dibenzyl and benzylbutyl dithiocarbamates of nickel(II) with P-ligands (unpublished results).

14. Husárek J.: Synthesis and structural characterization of the Ni(II) benzylbutyldithiocarbamate complexes with triphenylphosphine in the coordination sphere (unpublished results).
15. Přibil R.: Komplexometrické titrace, SNTL, Praha 1955, p. 22.
16. Geary W. J.: *Coord. Chem. Rev.* **7**, 81 (1971).
17. Tsipis C. A., Kessissoglou D. P. and Katsoulos G. A.: *Chim. Chron., New Ser.* **14**, 195 (1985).
18. Larionov S. V., Patrina L. A., Oglezneva I. M. and Uskov E. M.: *Koord. Chim.* **10**, 92 (1984).
19. Horák M. and Papoušek D.: Infračervená spektra a struktura molekul, Academia, Praha 1976, p. 340.
20. Lever A. B. P.: Inorganic Electronic Spectroscopy (2nd edit), Elsevier, Amsterdam 1984, p. 534.
21. Tsipis C. A., Kessissoglou D. P. and Manoussakis G. E.: *Inorg. Chim. Acta* **65**, L137 (1982).

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# VOLTAMMETRIC DETERMINATION OF THE LEAD, CADMIUM AND COPPER IN THE MUSCLES OF THE GREAT BREAM (*ABRAMIS BRAMA*)

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**Abstract**

The content of heavy metals (Pb, Cd, Cu) in muscles of the great bream (*Abramis brama*), was determined by anodic stripping voltammetry – the anodic oxidation after accumulation of the metals was observed by fast-scan differential pulse voltammetry (FSDPV). An analysis of fifteen fish samples was performed after dry mineralization procedure of their muscles. Using standard additions method the final values ranged in the interval 0.059-0.133 mg $kg^{-1}$ Pb, 0.002-0.049 mg $kg^{-1}$ Cd and 0.197-0.478 mg $kg^{-1}$ Cu. These values are under the hygienic limits of the Ministry of Health of the Czech Republic. In the appropriate fish habitat the metal contents in river water (7.52 μg $L^{-1}$ Pb, 1.94 μg $L^{-1}$ Cd, 12.93 μg $L^{-1}$ Cu) and in dried marsh sediment (5.12 mg $kg^{-1}$ Pb, 0.04 mg $kg^{-1}$ Cd, 4.93 mg $kg^{-1}$ Cu) were determined, too.

**Key words:** *heavy metals, fish muscle, anodic stripping voltammetry, differential pulse voltammetry*

## Introduction

An important habitat for sporting fishing is an abandoned meander of the river Moravia near Napajedla-town. In this place the river is embraced to the glen (called

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Napajedla-gate) by Chřiby-mountains and by Vizovice highland. This whole region was strongly affected by extreme floods in 1997. Rain washings from the fields and woody mountains and various pollutants were brought into riverine branch. The water transparency became evidently worse, colour of water gradually changed to more intensive brown-green shade, a marsh smell extended and an eutrophication was more and more evident. This resulted in the fear of unwholesomeness of fishes caught in this locality.

Pollutants, exhibiting various toxic effects on human organism[1], can get into mentioned water location by means of wastewater from tanning, electro technical or woodworking industry and also from agricultural activity. These substances can accumulate in sediments of river bed and thence they can pass into water flora and fauna as far as to man. Therefore the most suitable indicator of river pollution are fishes, because they are in water system on the end of the food web. The great bream (*Abramis brama*) was chosen which is extended in mentioned water locality and it is also relatively long-liver bentophagus.

There are several criteria for water quality valuation, one of them is the content of heavy metals. The most useful method for their determinations is an atomic absorption spectrometry (AAS) at the present time, but this technique was used as a referential one. The determination of copper, lead and cadmium was performed by anodic stripping voltammetry (ASV-DPV) with a hanging mercury drop electrode. This method is used much less in practice, but it is unpretentious economically, fast and very sensitive. Therefore it is recommended by Ministry of the Environment of the Czech Republic (technical regulate of the water system TNV 75 7389 / 2002) for determination heavy metals in various types of waters.

## Experimental

*Apparatus*

An analyzer Eko–Tribo–Polarograph (Polaro–Sensors, Prague) with a hanging mercury drop mini electrode (HMDE), a silver-silver chloride electrode in 3M-KCl, and an auxiliary Pt-electrode were employed for voltammetric measurements. An anodic oxidation of accumulated metals was watched by fast scan differential pulse voltammetry (FSDPV).
*Working parameters:* accumulation potential ($E_{acc}$) –0.7 V, accumulation time ($t_{acc}$) 40 s, rest time ($t_{rest}$) 10 s, potential range (at FSDPV-part) 0.85 V, scan rate 20 mV/s, pulse amplitude –50 mV and pulse width 100 ms.

pH was measured by a Präcitronic MV 870 pH-meter (Dresden, Germany) with combined glass and silver-silver chloride electrode. The pH-meter was calibrated by use of aqueous standard buffers (Institute of Sera and Vaccines, Prague). An apparatus Avanta Σ (GBC, Australia) was employed for the AAS as a control measurement.

*Chemicals and solutions*

Stock solutions of metal ions ($c$ = 0.001 mol $L^{-1}$) were prepared by dissolving of the dried chemicals purity p.a. (Lachema, Brno, Czech Republic). The nitric acid for mineralization finishing and for transfer of the residue into the solution was purity Analpur SD (Analytika, Prague). A pork liver (Food Detection Science Institute Ministry of Commerence Beijing, China) GBW 08551 was used as a certificated referential stuff for verification of the voltammetric method applicability on real samples. Ultra pure water (ELGA, Ltd. GB) was used throughout in all experiments.

*Sampling and treatment*

Sampling of the great breams was carried out by catching fishes on rod laid on the bottom of the river. On the whole 25 fishes were caught approximately the same lengths (24-30 cm), weight (200-300 g) and age of about 5 years. Fifteen samples of bream were randomly selected for the analysis. The caught fishes were peeled off, got rid of fins, head and entrails and a muscle was frozen and stored in polyethylen bags and preserved to analysis time. After the thawing a part of muscle from dorsal parts was scarped, weighed and mineralized.

A microwave mineralization on an apparatus Uniclever BM-1 (Plazmatronika, Poland) that is currently used at the AAS method didn't appear to be suitable for a voltammetric trace analysis. The obtained product exhibited the incomplete sample destruction even after double mineralization and with addition of $H_2O_2$. Voltammetric peaks presented an extended form and deformations. For this reason we approached the classical dry mineralization, unfortunately time-consuming method.

*Procedure:* In porcelain crucible weighed muscle (1-2 g) was burned in electric furnace at three temperatures – for two hours at 150 °C, further two hours at 250 °C and sixteen hours at 450 °C. After temperature reduction 1 ml concentrated nitric acid was added, then the sample was evaporated to dryness and burned in furnace again for two hours at 450 °C. A dove-coloured ash obtained was dissolved in 5 ml 1% $HNO_3$ by means of sonic bath. After dilution with ultra pure water the sample was prepared for the voltammetric analysis. Samples of metal standards were parallelly subjected to the identical procedure.

**Results and discussion**

The sample with supporting electrolyte (0.1M-$HNO_3$) in an electrochemical cell was deaerated by passage of a nitrogen stream for minimally 5 min. The measured solution was again bubbled by nitrogen for 2 minutes always after each addition of a metal standard. During the analysis the analysed solution was kept under the inert atmosphere. Recorded ASV-FSDPV curves show separated anodic peaks of analysed metals (-0.50 V Cd, -0,34 V Pb, +0.06 V Cu) and they are suitable for analytical use (Fig. 1). Determination of each metal in five parallelly mineralized muscle samples of each fish was performed using the method of standard additions (Fig. 2). In parallel with them were recorded also mineralized samples of standards and model blind experiments

without the fish muscle. Copper shows little solubility in mercury in acidic medium[2], therefore its standard addition was always brought as the last component into the measured solution. Results of the metal determinations were converted to the metal contents in 1 kg of fish muscle (Table 1).

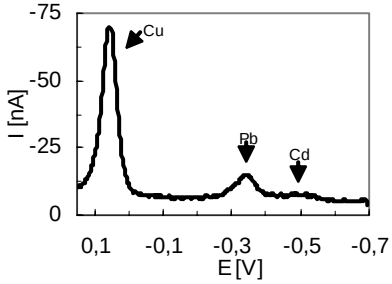


**Fig. 1.** ASV-FSDP- voltammogram of the metal mixture in 0.1M-$HNO_3$, $E_{acc}$ –0.7 V, $t_{acc}$ 40 s, $t_{rest}$ 10 s, scan rate 20 mV/s, pulse amplitude –50 mV

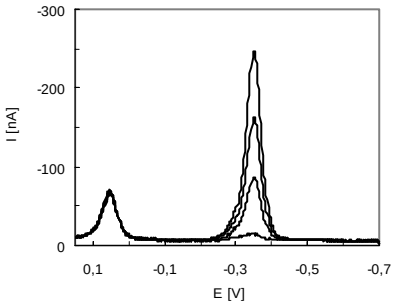


**Fig. 2.** Lead determination by means of standard additions method in 0.1M-$HNO_3$ $E_{acc}$ –0.7 V, $t_{acc}$ 40 s, $t_{rest}$ 10 s, scan rate 20 mV/s, pulse amplitude –50 mV; sample with three successive additions (always 10 μL) of 0.001M-$Pb^{2+}$

**Table 1.** Determined content of lead, cadmium and copper in muscle of the great bream (*Abramis brama*)

(15 fishes, their length 25-30 cm, results with 95% probability)

| | Reliability interval $\bar{x} \pm s_{\bar{x}} \cdot t_\alpha$ | Median |
|---|---|---|
| Pb [mg/kg] | 0.081±0.016 | 0.075 |
| Cd [mg/kg] | 0.028±0.009 | 0.029 |
| Cu [mg/kg] | 0.337±0.045 | 0.317 |

All results have the normal distribution, none of them is outlier; $\bar{x}$ - mean of results, $s_{\bar{x}}$ - standard deviation of the mean, $t_\alpha$ - criterion of the Student's distribution

The determined contents of monitored metals in bream muscle were very low. In the case of lead interval 0.059-0.133 mg $kg^{-1}$ was found. None of fifteen analysed samples achieved the hygienic limit[3] (0.2 mg $kg^{-1}$), although the dried marsh sediment from river bottom contained expressively higher amount of lead (5.12 mg $kg^{-1}$). The $Pb^{2+}$–concentration in river water of the given locality was only $7.52 \times 10^{-3}$ mg $L^{-1}$. We came to a conclusion that the lead-ion is bounded in a form of a small soluble complex or precipitate in sediment.

Cadmium is the most toxic metal from the monitored metal ions. That's why the sanitary standard[3] permits only 0.05 mg $kg^{-1}$ of cadmium in a fish muscle. This value was only slightly exceeded at one sample (0.052 mg $kg^{-1}$, that is 4% upwards) and at two next samples the metal content (0.049 and 0.047 mg $kg^{-1}$) was closely under the limit. The determined values of other twelve samples occurred in an interval 0.002-0.039 mg $kg^{-1}$. These small values are in accord with the content of cadmium in dried sediment (0.04 mg $kg^{-1}$) and in river water ($1.94 \times 10^{-3}$ mg $L^{-1}$).

A quite troublefree case in fish muscle is also the content of copper. Its concentration in river water was $12.93 \times 10^{-3}$ mg $L^{-1}$ and in river bottom sediment was found 4.93 mg $kg^{-1}$. Amounts of the metal determined in fish muscle (0.197-0.478 mg $kg^{-1}$) correspond to these values and they are deep below limit[3] (10 mg $kg^{-1}$).

The most commonly used AAS-method for determination of heavy metal provided analogous results of control samples. Nevertheless owing to very low contents of monitored metals not only in the fish muscle but also in river water and in marsh sediment the voltammetric procedure with a combination of the dry mineralization was performed to verify the used method. A pork liver GBW 08551 was used as a certificated referential stuff for verification of the voltammetric method applied to real samples, the declared content of lead was 0.54±0.04 μg/g and for cadmium 0.067±0.004 μg/g. Three samples of liver in range 750-1000 mg were weighed for voltammetric determination (ASV-DPV) and they were mineralised and adapted for analysis of above-mentioned process. It was found 0.53±0.05 μg $g^{-1}$ Pb and 0.066±0.007 μg $g^{-1}$ Cd (calculation by means of average results $\bar{x}$ and standard deviation of mean $s_{\bar{x}}$). From these results and from t-criteria calculated for $\alpha = 0.05$ follows that the voltammetric method used for determination of heavy metals (Pb, Cd) in the certificated referential stuff as well as in the fish muscle is suitable.

## Conclusion

The voltammetric method (ASV-FSDPV) with hanging mercury mini electrode was used for determination of lead, cadmium and copper in a muscle of the great bream (*Abramis brama*). A decomposition of the organic fish samples was performed by dry mineralization. The metal determination was realized by means of anodic stripping analysis in milieu 0.1M-$HNO_3$, the method of standard additions was used. All samples of muscle of the fifteen fishes exhibited very low contents of monitored metals and with the exception of only one cadmium sample they didn't reached the hygienic limits[3], which are valid in the Czech Republic. On the basis of the found data it is possible assume that mentioned metals do not increase a health hazard at the consummation of fishes caught in the followed locality. The bad sensorial quality of river water in the abandoned meander will be undoubtedly caused by organic components.

From results it also follows that anodic stripping voltammetry with fast scan differential pulse detection (ASV-FSDPV) can be an alternative method for determination of small or trace metal contents in river water because it is very sensitive, accurate, fast and unpretentious economically.

## References

1. Kavka Z., Punčochářová J.: *Chem. Listy* **96**, 611 (2002).
2. Kalvoda R.: Elektroanalytická chemie životního prostředí. SNTL, Prague 1985.
3. Ministry of Health of the Czech Republic: Public notice No.53/2002 Sb.

Acta Univ. Palacki. Olomuc.
Fac. rer. nat. 2004
Chemica 43, 88-93

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# NICKEL AND COPPER COMPLEXES WITH BENZENE-1,2-DITHIOL AND SELECTED N,P-LIGANDS

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**Abstract**

New nickel and copper dithiolate complexes of composition [Ni(phen)(bdt)] (**I**), [Ni(n-phen)(bdt)] (**II**), [Ni(ch)(bdt)] (**III**), [Cu(ch)(bdt)] (**IV**), [Ni(en)(bdt)] (**V**), $[Ni(PPh_3)_2(bdt)]$ (**VI**), $[Ni_2(but_3P)_2(bdt)_2]$ (**VII**) (bdt = benzene-1,2-dithiol, phen = phenanthroline, n-phen = 5-nitro-1,10-phenanthroline, ch = 1,2-cyclohexanediamine, en = ethylenediamine, $PPh_3$ = triphenylphosphine, $but_3P$ = tributylphosphine) have been synthesized and studied by physico-chemical methods such as elemental analysis, IR and electron spectroscopy, magnetochemical and conductivity measurements.

**Key Words:** *Nickel, copper benzene-1,2-dithiolates, synthesis, physico-chemical study*

## Introduction

Bis(dithiolene) metal complexes have been receiving a great attention for developing new materials due to their multipurpose properties such as electrical conductivity, strong near-IR absorption, molecular magnetism and catalytic applications[1-4]. We have described syntheses and properties of nickel, cobalt and copper complexes of composition $R[M(bdt)_2]$: M = Ni, Co, Cu and R = $Me_4N$, $Et_4N$, $Pr_4N$, $Me_3PhN$, $MePh_3P$, $Ph_4P$ with *benzene-1,2-dithiol (bdt) in the coordination sphere[5]. In

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the case of $(MePh_3P)[M(bdt)_2]$; M = Ni, Co, Cu, X-ray structural analysis confirmed a slightly distorted square coordination arrangement around central atoms.

The aim of this work is the synthesis and characterization of Ni and Cu benzene-1,2-dithiolate complexes with selected bidentate nitrogen and monodentate phosphorus donor ligands.

## Materials and methods

$NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and methanol were from Lachema Brno, remaining reagents were produced by Fluka, all of "p.a." purity.

The content of nickel and copper was determined by chelatometric titration on murexid as indicator[6]. C, H, N, analyses were performed on an EA 1108 instrument (Fisons). Magnetic susceptibilities were measured by the Faraday method using $Co[Hg(NCS)_4]$ as a calibrant on a laboratory-designed instrument with a Leybold-Heraeus cryostat and a Sartorius 4434 MP-8 microbalance. Diamagnetic corrections were made using Pascal constants[7]. Conductivities were measured with a Conductivity Meter OK 102/1 (Radelkis Budapest) at 25 °C. Diffuse-reflectance electronic absorption spectra (45000-11000 $cm^{-1}$) were carried out on a Specord M 40 and IR spectra (4000-400 $cm^{-1}$) were recorded on a Specord M 80 (Carl Zeiss, Jena) using nujol mulls.

*Syntheses of complexes*

Compounds [Ni(phen)(bdt)] (**I**) and [Ni(n-phen)(bdt)] (**II**) were prepared as follows: To the methanol solution (10 $cm^3$) of $NiCl_2 \cdot 6H_2O$ (1 mmol) was added a warm solution of the relevant ligand (phen, n-phen) (2 mmol in 10 $cm^3$ methanol) and the mixture was stirred. After addition of benzene-1,2-dithiol (1 mmol) in 10 $cm^3$ methanol and triethylamine (2 mmol), which was slowly dropped into the suspension, a precipitate was formed during 8 hours of stirring the precipitate formed. It was filtered, washed with methanol and dried under an infra-lamp at 40ºC.

Complexes [M(ch)(bdt)] (**III**,**IV**) (M = Ni, Cu) were synthesized analogically using 1,2-cyclohexanediamine (2 mmol) as N,N-ligand. For the [Ni(en)(bdt)] complex (**V**), ethylenediamine (2 mmol) was used.

Complexes $[Ni(PPh_3)_2(bdt)]$ (**VI**) and $[Ni_2(but_3P)_2(bdt)_2]$ (**VII**) were formed by stirring methanol solutions (10 $cm^3$) of $NiCl_2 \cdot 6H_2O$ and an appropriate ligand ($PPh_3$, $but_3P$)
(2 mmol) with benzene-1,2-dithiol (1 mmol) in 10 $cm^3$ methanol. Triethylamine (2 mmol) was added to this mixture and after 10 hours the resulting precipitate was filtered, washed thoroughly with methanol and dried under an infra-lamp at 40ºC. In the case of (**VII**), the reaction was carried out under nitrogen; the re-crystallization from hot acetone to provide crystals suitable for X-ray analysis was unsuccessful, since the crystals were too small.

## Results and discussion

The elemental analyses are listed in Table 1, the physico-chemical results are given in Table 2.

**Table 1.** Elemental analyses of prepared compounds

| Compound | Calc./found (%) | | | |
|---|---|---|---|---|
| | C | H | N | Ni, Co, Cu |
| I. [Ni(phen)(bdt)] | 57.02/56.15 | 3.19/2.95 | 7.39/6.33 | 15.48/ - |
| II. [Ni(n-phen)(bdt)] | 50.97/51.05 | 2.61/2.29 | 9.91/9.62 | 13.84/14.11 |
| III. [Ni(ch)(bdt)] | 46.03/46.28 | 5.79/5.57 | 8.95/8.67 | 18.75/19.12 |
| IV. [Cu(ch)(bdt)] | 45.33/45.42 | 5.71/5.56 | 8.81/8.79 | 19.99/20.22 |
| V. [Ni(en)(bdt)] | 37.10/37.06 | 4.67/4.25 | 10.82/11.46 | 22.66/22.95 |
| VI. [Ni(PPh3)2(bdt)] | 69.72/68.31 | 4.74/4.37 | - | 8.11/8.38 |
| VII.[Ni2(but3P)2(bdt)2] | 53.88/53.39 | 7.79/7.95 | - | 14.63/15.16 |

**Table 2.** Results of physico-chemical measurements

| Comp. | $\mu_{eff}$ (BM) | UV/VIS (x $10^3$ $cm^{-1}$) | | | | IR ($cm^{-1}$) | | | | | $\lambda_M$ ($S.cm^2.mol^{-1}$)[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | ν(C-S) | ν(C-N-C) | ν(C-S) | δ(C-P) | | |
| I | dia | 17.8 | 22.3 | 26 | 37 | 840s | 1144w | 1280m | - | - | 1.0 |
| II | dia | 18.5 | - | - | 37.5 | 844s | 1144m | 1284m | - | - | 0 |
| III | dia | - | 22 | 29 | 37.5 | 850w | - | 1276s | - | - | i |
| IV | 1.81 | 17 | 24 | - | - | 840w | - | 1256s | - | - | 0 |
| V | 0.97 | - | 22 | 29 | 37 | 840w | - | 1268s | - | - | 4.6 |
| VI | dia | 17 | 25 | 32 | - | 848m | - | 1282m | 1096m | 694s | 17.4 |
| VII | dia | 17 | 23.5 | 27.5 | 35.3 | 840w | - | - | 1080m | 668m | 0.4 |

[a] In dimethylformamide solution (c = $10^{-3}$ $mol.dm^{-3}$); i - insoluble

For nickel complexes, from magnetochemical measurements follows that all complexes except for **V** are diamagnetic. This fact implies square planar coordination of central nickel atom (the slightly higher $\mu_{eff}$ value of **V** can be explained by the presence of an analytically non detectable paramagnetic species). This assumption is also supported by electron spectroscopy (maxima between 17000-22000 $cm^{-1}$ and 23000-29000 $cm^{-1}$ belonging to the $^1A_{1g} - {}^1A_{2g}$ and $^1A_{1g} - {}^1B_{1g}$ transitions; over 35000 $cm^{-1}$ due to the CT-transitions) and conductivity measurements (all compounds are non-electrolytes[8]). For compound **VII**, we assume a binuclear nickel complex with two $NiS_2P_2$ chromophores and two $but_3P$ bridges. This conclusion should be proved by X-ray structural analysis, but all our attempts to obtain crystals suitable for this purpose were unsuccessful.

For the Cu-complex **IV** with one unpaired electron we assume similar arrangement of coordination sphere to the nickel complex **V**.

All complexes **I-VII** exhibit IR peaks typical of dithiolates[9]: ν(C-S): 840-850 $cm^{-1}$ and 1250-1284 $cm^{-1}$. For compounds with (n)-phen **I-II**, the ν(C-N-C) vibrations between 1130-1144 $cm^{-1}$; for complexes containing $PR_3$ (**VI, VII**), the δ vibrations (C-P) at 1080-1096 $cm^{-1}$ and 668-694 $cm^{-1}$ were recorded.

## References


1. Ha-Jin L. and Dong-Youn N.: *Polyhedron* **19**, 425-429 (2000).
2. Mueller-Westerhoff U.T. and Vance B.: *Comp. Coord. Chem.* **2**, 595 (1987).
3. Olk R.M., Olk B., Dietzsch W., Kirmse R. and Hoyer E.: *Coord. Chem. Rev.* **117**, 99 (1992).
4. Cassoux P., Valade L., Kobayashi H., Kobayashi A., Clark R.A. and Underhill A. E.: *Coord. Chem. Rev.* **110**, 115 (1991).
5. Mrkvová K., Kameníček J., Šindelář Z., Kvítek L., Mrozinski J., Nahorska M. and Žák Z.: *Trans. Met. Chem.* **29**, 238 (2003).
6. Přibil R.: Komplexometrické titrace, SNTL Praha 1985.
7. Bourdeaux E. A. and Mulay L. N.: *Theory and Applications of Molecular Paramagnetism*, Wiley New York 1976, p. 491.
8. Geary W.J.: *Coord. Chem. Rev.* **7**, 81 (1971).
9. Pouchert C.J.: The Aldrich Library of Infrared Spectra, Milwaukee Wisconsin 1981.



Acta Univ. Palacki. Olomuc.
Fac. rer. nat. 2004
Chemica 43, 94-97

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# ANOTHER LOOK AT BASICITY EFFECTS INTERPRETATION IN THE HBD-HBA CONCEPT OF ACIDS AND BASES

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**Abstract**

Some problems connected with evaluation of basicity effect on chemical properties and processes, viz.(i) number of basicity characteristics necessary, (ii) bulk and monomer hydrogen bond basicities, (iii) only familiar dependences observed in some cases, and (iiii) behaviour of some classes of compounds as trialkylamines and pyridines may be understand from point of view of nonspecific interactions effects on properties of H-bond complexes in solutions. In the sense of LFER the vapor state equilibrium constants of the formation of H-bond complexes between 4-fluorophenol and 10 bases and sensitivity of the log K to the nonspecific interactions were calculated. Compatibility of the presented procedure and the Maria, Gal, Franceschi, Fargin procedure of $F_1$, $F_2$ factors[8] is stated and proposed for the evaluation of the basicity characteristics of both the methods.

**Key Words:** *HBA-basicity, 4-fluorphenol complexes, vapor state equilibrium constants*

## Introduction

HBD-HBA - Hydrogen Bond Donor – Hydrogen Bond Acceptor definition of acids and bases has originated during last 40 years and officially was introduced into chemistry by Abraham, Doherty, Kamlet and Taft in 1986 (A new look at acids and bases)[1]. HBA – basicity of a compound is in this conception considered as a capability of the compound to affect a **B**asicity **D**ependent **P**roperty (BDP) of an acid through

hydrogen bond formed between the electron donating base and a hydrogen of the acid. Among the most studied BDP have belonged equilibrium constants of the H-bond complexes formation, UV-VIS, IR and NMR spectra. The dominant position among the equilibrium studies belongs to the interaction of 4-fluorophenol with bases in the sense of the equation

$$4\text{-F-}C_6H_4OH + B = 4\text{-F-}C_6H_4OH\ldots.B \quad (1)$$

characterized by the equilibrium constant K:

$$K = [4\text{-F-}C_6H_4OH...B] / [4\text{-}C_6H_4OH] .[B] \quad (2)$$

These equilibrium constants have been determined by calorimetric, ir and $^{19}$F-NMR methods and excellent agreement of the results obtained was concluded[2].

An increased interest in the understanding the basicity effects has been provoked by a great importance of the HBA basicity in chemical and especially biological processes, see e.g.[3-6].

Among critical problems of the HBA basicity evaluations have belonged number of the basicity characteristics necessary for the description of basicity effects (i), significant differences between bulk and monomer HBA basicities (ii), failures which have been met with evaluation of the basicity effect of some classes of bases as trialkylamines, pyridines or nitriles (iii) and observation of only family LFER dependences in the interactions of various groups of bases with different HBD acids (iiii).

The purpose of this paper is to classify these problems by help of the model of the effect of nonspecific interactions between medium and HBD-HBA complexes.

**Results and discussion**

As stated above the H-bond complex formation between 4-fluorophenol and various bases has a leading position between the HBA basicity studies performed till now. The log K values for about 500 these H-bond complexes obtained predominantly in tetrachloromethane solutions have been published[3] and are considered as the most extensive scale of HBA basicities. Besides the scale a great number of other basicity characteristics have been proposed up to now. It was not only because of the basicity is a fundamental chemical property, but no doubt also due to the HBA basicity can be measured relatively easily and there are a great number of on basicity dependent chemical properties (BDP).

The present model is based on the dependence of the properties (log K here) of H-bond complex formed between a HBD acid (4-fluorophenol here) and HBA bases on nonspecific interactions of the complex in a solution. Thus the 4-fluorophenol and any HBD acid in general, interacts with HBA bases through hydrogen bonding in vapor phase (ideal gas approximation) according to equation (1). In the vapor state depends the equilibrium constant K (equation 2) as well as other properties of the H-bond complex on the HBA basicity of a base only. If the interaction takes place in a medium (**S**), where

only nonspecific interactions between the **S** molecules and the H-bond complex can be realized, the BDP including the log K are affected by these interactions and should obey in the sense LFER principle the simple equation

$$BDP^S = BDP^g + p \times P \qquad (3)$$

where **P** is a characteristics of the medium ability for nonspecific interactions and p is the sensitivity of the $BDP^S$ towards the **P.** From the $BDP^S$ obtained in various media of known **P** the $BDP^g$ and **p** may be estimated. From the model it may be obvious that if the **p** highly differ for the media applied it can not be expected to be sufficient a characterization of the bases by only one characteristics, that there shall be different effects of bases if applied as solute or as the solvent and even different basicity effect of some bases in media of
different **P**.

To test the applicability and usefulness of the model the equation (3) was applied to experimental data on the effect of medium on log K of the H-bond complex formation between 4-fluorophenol and ten bases determined in six media of various **P**[2,9]. As the medium characteristics **P** the effective Born functions of relative permittivity $\mathbf{W_B}$[7] were used. $\mathbf{W_B}$ are for most solvents near to the Born functions of relative permittivity ($\varepsilon_r$), $f(\varepsilon_r) = (\varepsilon_r-1)/\varepsilon_r$ and for vapor state is $W_B = f(\varepsilon_r) = 0.00$. The experimental data used as well as the $W_B$ and results of the regression analysis according the equation (3) are given in the table 1.

The correlations performed are satisfactory. The table points to fairly higher differences in log $K^g$ as compared with those obtained in media used and highly different **p** for some of the bases studied, the largest difference being between the **p** for hexamethylphosphoramide and triethylamine. The results point to two facts – the basicity and nonspecific interactions act in the opposite directions – the polarity effects reduce the basicity effects and the order of basicity of some bases obtained in various media is different. For the five bases, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), pyridine (Py), cyclohexanone (CHON), and triethylamine ($Et_3N$) the following orders of their basicities in the media studied are found:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Vapor state: | DMSO | > | DMF | > | Py | > | CHON | > $Et_3N$ |
| Tetrachormethan | DMSO | > | DMF | > | $Et_3N$ | > | Py | > CHON |
| o.Dichlorobenzen | DMSO | > | $Et_3N$ | > | DMF | > | Py | > CHON |
| 1,2-Dichloroethane (or bulk state) | $Et_3N$ | > | DMSO | > | Py | > | DMF | > CHON |

**Table 1**
Medium effect on the equilibrium constants K of the complex formation between 4-fluorophenol and ten bases and results of the regression analysis of the data by the equation (3).

| Medium | log K | | | | | | | | | | $W_B$[7] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Base | I | II | III | IV | V | VI | VII | VIII | IX | X | |
| Cyclohexane | 1.99 | 2.03 | - | 2.30 | 2.56 | 3.80 | 0.83 | 1.00 | 3.15 | 1.42 | 0.49 |
| Tetrachloromethane | 1.93 | 1.88 | 1.32 | 2.06 | 2.53 | 3.56 | 0.71 | 0.79 | 2.81 | - | 0.58 |
| Chlorobenzene | 1.84 | 1.60 | - | 1.74 | 2.20 | 3.06 | 0.55 | 0.48 | 2.38 | 1.06 | 0.76 |
| o-Dichlorobenzene | 1.93 | 1.63 | 1.02 | 1.70 | 2.18 | 3.06 | 0.45 | 0.39 | 2.61 | 0.95 | 0.80 |
| 1,2-Dichloroethane | 1.70 | 1.29 | 0.52 | 1.27 | 1.65 | 2.55 | 0.09 | 0.15 | 2.14 | 0.72 | 0.93 |
| Dichloromethane | 1.67 | 1.26 | 0.50 | 1.18 | 1.44 | 2.37 | 0.14 | - | 2.10 | - | 0.92 |
| $BDP^g \equiv \log K^g$ | 2.33 | 2.88 | 2.75 | 3.49 | 3.87 | 5.33 | 1.67 | 2.23 | 4.16 | 2.21 | 0.00 |
| $-p \equiv -d(\log K)/dW_B$ | 0.65 | 1.69 | 2.37 | 2.38 | 2.38 | 3.03 | 1.62 | 2.43 | 2.18 | 1.57 | |
| Correlation coeff. | .879 | .983 | .962 | .982 | .928 | .981 | .969 | .976 | .959 | .994 | |

The bases:I – triethylamine, II – pyridine, III – cyclohexanone, IV – N,N-dimethylformamide, **V –** dimethyl sulfoxide, VI – hexamethylphosphoramide, VII – 1,4-dioxane, VIII – benzonitrile, IX – 4-N,N-dimethylpyridine, X – 4-bromopyridine

It seems therefore something hazardous to state values of some properties obtained in a medium as general solvent or solute basicity characteristics and as a more suitable seems to be for such purpose the $BDP^g$ obtained by extrapolation from medium dependences of the $BDP^S$.

Of interest seems to be the relation of the log K and p to the $F_1$ and $F_2$ factors obtained by multivariate analysis, here by the method of principal components[8]. These F factors were calculated as principal components of general HBA basicity effects for 22 bases and of the 10 bases whose medium affecting is known, for the 7 bases are known. The correlation equations between these F factors and $\log K^g$ and **p** have the form

$$F_1 = 0.156 + 0.857 \times \mathbf{p} + 0.549 \times \log K^g \qquad R = 0.986 \qquad (4)$$

$$F_2 = -0.586 - 0.149 \times \mathbf{p} + 0.099 \times \log K^g \qquad R = 0.992 \qquad (5)$$

**Table 2**
Equlibrium constants of the 1:1 complex formation of 4-fluorophenol with 22 bases (log $K^g$) in vapor state and sensitivity of the log K to medium polarity (p) estimated from the $F_1$ and $F_2$.

| Base | $F_1$ | $F_2$ | $\log K^{CCl_4}$ | $\log K^g$ | $-p \equiv -d(\log K)/dW_B$ |
|---|---|---|---|---|---|
| 1. Nitrobenzene | -0.89 | 0.01 | 0.73 | 2.11 | 2.38 |
| 2. Acetonitrile | -0.57 | -0.04 | 0.90 | 2.15 | 2.69 |
| 3. Diethyl carbonate | -0.52 | -0.02 | 1.00 | 2.30 | 2.24 |
| 4. 1,4-Dioxane | -0.37 | -0.16 | 0.71 | 1.72 (1.67) | 1.74 (1.62) |
| 5. Ethyl acetate | -0.44 | -0.02 | 1.09 | 2.37 | 2.21 |
| 6. Acetone | -0.37 | -0.02 | 1.18 | 2.44 | 2.17 |
| 7.Cyclohexanone | -0.34 | 0.01 | 1.32 | 2.75 (2.75) | 2.47 (2.37) |
| 8. Diethyl ether | -0.29 | -0.11 | 1.01 | 2.05 | 1.79 |

The continuation of Table 2

| | | | | | |
|---|---|---|---|---|---|
| 9. Trimethyl phosphate | -0.08 | 0.24 | 2.45 | 4.03 | 2.72 |
| 10. Tetrahydrofuran | -0.21 | -0.04 | 1.26 | 2.48 | 2.10 |
| 11. 2,6-Dimethylpyridine | 0.47 | -0.10 | 2.13 | 2.80 | 1.16 |
| 12. 2,4,6-Trimethylpyridine | 0.53 | -0.07 | 2.29 | 3.00 | 1.22 |
| 13. Dimethyl sulfoxide | 0.15 | 0.20 | 2.53 | 4.03 (3.87) | 2.59 (2.38) |
| 14. Tetramethylurea | 0.20 | 0.11 | 2.30 | 3.62 | 2.28 |
| 15. N,N-Dimethylaniline | 0.11 | -0.40 | 0.45 | 0.93 | 0.83 |
| 16. N,N-Dimethylformamide | 0.05 | 0.12 | 2.06 | 3.53 (3.49) | 2.53 (2.38) |
| 17. N,N-Dimethylacetamide | 0.18 | 0.15 | 2.38 | 3.81 | 2.47 |
| 18. N-Methylpyrrolidone | 0.15 | 0.16 | 2.37 | 3.83 | 2.53 |
| 19. Hexamethylphosphoramide | 0.48 | 0.38 | 3.56 | 5.25 (5.33) | 2.88 (3.03) |
| 20. Pyridine | 0.42 | -0.08 | 1.88 | 2.85 (2.88) | 1.67 (1.69) |
| 21. 4-Methylpyridine | 0.49 | -0.05 | 2.03 | 3.07 | 1.79 |
| 22. Triethylamine | 0.85 | -0.26 | 1.93 | 2.33 (2.33) | 0.69 (0.65) |

Values of log $K^g$ and –p in the brackets are those calculated by the equation (3)
$F_1$ and $F_2$ factors taken from[8], log $K^{CCl_4}$ taken from [9, 2].

These correlations carried with seven solvents of known both **p** and log $K^g$ and $F_1$ and $F_2$ factors entitle the model proposed. Moreover the mutual dependences between these characteristics make possible to estimate the log $K^g$ and **p** from the F factors and vice versa. Thus from the correlation of the log $K^g$ and the F factors and known – mostly published values of log $K^{CCl_4}$ the log $K^g$ and **p** can be calculated using the equations ($W_B^{CCl_4} = 0.58$):

$$\log K^g = 2.87 + 0.91 \times F_1 + 5.10 \times F_2 \qquad R = 0.997 \qquad (6)$$

$$\mathbf{p} = (\log K^{CCl_4} - \log K^g) / 0.58 \qquad (7)$$

Results of such estimations of the log $K^g$ and **p** are for the set of all the 22 solvents of known F factors given in the table 2. Obtained log $K^g$ and **p** for the seven solvents where both the procedures were applied exhibit fair agreement and clearly differentiate the solvents according to their **p** values into familiar sets.e.g. 0.6 – 1.0 ($Et_3N$, N,N-dimethylaniline), 1.0 – 1.8 (pyridines), 1.8 – 2.6 (most of solvents), 2.6 – 3.1 (phosphates, acetonitrile). The performed analyses of the medium effects of nonspecific interactions on properties of H-bond complexes interpret some problems of the basicity effects evaluations and probably makes the procedures less hazardous[10].

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## References


1. Abraham M. H., Doherty R. M., Kamlet M. J., Taft R. W.: *Chemistry in Britain* **22,** 551 (1986).
2. Gurka D., Taft R. W.: *J. Amer. Chem. Soc.* **91,** 4794 (1969).
3. Abraham M. H., Grellier P. L., Prior D. V., Morris J. J., Taylor P. J.*: J. Chem. Soc., Perkin Trans.2*, **1990**, 521.
4. Abraham M. J.: European J.: *Medical Chem*. **39,** 235 (2004).
5. Agrawat V. K., Chaturwedi S., Abraham M. H., Khadikar P. V.: *Bioorg. Med. Chem*. **11,** 4523 (2003).
6. Cometto-Muniz J. E., Cain W. S., Abraham M. H.: *Chem. Senses* **28,** 467 (2003).
7. Bekárek V.;. Nevěčná T. Rozpouštědlové vlivy v chemii a jejich hodnocení, ACADEMIA, Praha, **1992.**
8. Maria P. –C., Gal J. –F., Franceschi J., Fargin E.: *J. Amer. Chem. Soc.* **109,** 483 (1987).
9. Abraham M. H., Grellier P. L., Prior D. V., Morris J. J., Taylor P. J., Maria P. –C., Gal J. –F.: *J. Phys. Org. Chem.* **2**, 243 (1989).
10. Abraham M. H., Buist G. J., Grellier P. L., McGill R. A., Prior D. V., Oliver S., Turner E., Morris J. J., Taylor P. J., Nicolet P., Maria P. Ch., Gal J. –F., Abboud J. –L, M., Doherty R. M., Kamlet M. J., Shuely W. J., Taft R. W.: *J. Phys. Org. Chem.* **2,** 540 (1989).



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# FLUORIDE DETERMINATION IN URINE WITH ION SELECTIVE ELECTODE: WITHIN LABORATORY METHOD AND SAMPLE STORAGE OPTIMIZATION

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**Abstract**

This work presents method validation of fluoride determination in urine of children. The fluoride ion selective electrode and silver chloride reference electrode have been used for all measurements. We have found that described method is accurate (average recovery 98.4 %) and provided precision RSD = 2.8 %. The evaluated value of limit of detection using direct signal method has been $3.2.10^{-6}$ $mol.l^{-1}$. The fluoride concentration in real urine samples is influenced during the storage in the refrigerator (+ 4 °C). The samples should be stored deeply frozen at – 20 °C before the analysis. The comparison of several buffers (commercially available TISAB, citrate buffer with different pH and citrate buffer with NaCl) leads to the conclusion that there is no significant difference among used buffer solutions.

**Key Words:** *fluoride, urine, method validation and sample storage*

## Introduction

Monitoring of fluoride urine levels (fluoride excretion) in children together with exactly or at least approximately determined daily fluoride intake into human body can

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be used in clinical praxis for the prophylaxis of the tooth decay. We have looked for a method of fluoride determination that can be used in dentist practice and is relatively cheap. The fluoride concentrations in urine can be quite easily and fastly measured potentiometrically with use of a selective fluoride electrode, which have been described in several publications[1,2]. We have chosen this method (using fluoride ion selective electrode – ISE) and validated following parameters for real samples: accuracy (recovery testing), precision, suitability of linear and quadratic calibration models, limits of detection and quantification. The cations such as calcium, magnesium, iron, aluminium and pH > 8 can cause interferences[3] so we studied the influence of several buffer solutions. The formation of sediment during storage of urine samples at – 18 °C has been described[4] and observed in our work so we tested the possibilities to store urine samples at + 4 °C in refrigerator and – 20 °C in freezer.

During last years some developments in using ISE for fluoride determination were achieved. Itai and Tsunoda[2] developed an apparatus for flow injection analysis (FIA) for rapid determination of very low fluoride concentrations in body fluids such as serum and urine. All interferences caused by serum and urine matrices were eliminated using the proposed method. In the interference study carried out by Frenzel and Brätter[5] the authors focused on the influence of parameters such as ionic strength, viscosity and pH on FIA with fluoride ISE. All measurements were made with the wall-jet electrode and their results demonstrate the significance of considering the sample composition in preventing interferences in flow-injection potentiometry. The use of commercially available TISAB and TISAB containing CDTA is also discussed. Commercially available TISAB was described as unsuitable for the analysis of undiluted tea and urine samples[6]. A rapid and sensitive analytical procedure based on chemiluminiscence detection[7] is described for the determination of free fluoride at sub-nanogram levels in water and human urine by use of controlled-reagent-release technology in a FIA system. The analytical reagents used for chemiluminiscence reaction (luminol and periodate) were immobilized on anion-exchange resins in flow injection system and through water and sample injection were eluted from the anion exchange column to generate the chemiluminiscence.

There are some other methods of fluoride determination described in the literature even if using ISE belongs to the most popular and most widely used approaches because of its simplicity and low cost. In the 1960's many spectrophotometric methods using complex formation have been described[8]. Two of these methods for water analysis have been widely used in the Czech laboratories because of their standardization in the Czech technical standards system (CSN 830520)[9]. Spectrophotometric method with zirconium alizarin complex was used as the arbitral one and chelate complex formation with xylene orange could also be applied. The fluoride determination in urine with these two methods suffers from the interferences arising from urine matrix. The spectrophotometric methods usually require long time preparation of reagents and samples and nowadays are not widely used in the laboratories.

It is also possible to use separation methods such as gas chromatography (GC), ion chromatography (IC) and capillary zone electrophoresis (CZE) for fluoride determination in biological samples. The comparison of GC and ISE method[10] for measuring fluoride in urine showed that GC method underestimates the true level of

fluoride because trimethylchlorosilane used for combining with fluoride does not bind all the available fluoride. The authors concluded that the GC method is up to 3 times less effective than ISE one for measuring fluoride in urine. When fluoride concentrations in biological specimens is determined, the GC method may produce artificially low results, which require further verification. Michigami et al.[11] developed an ion chromatographic method for the determination of trace amounts of free urinary fluoride, using ODS column dynamically coated with cetyl-n-butylammonium bromide. The inorganic and organic anions commonly found in urine had a little effect on the determination of fluoride. Several studies[12,13] have reported a method for the determination anions by CZE with indirect UV detection. The anions mixture containing bromides, chlorides, fluorides, nitrites and some others were separated in buffer containing ammonium dichromate, ammonium acetate, diethylenetriamine and methanol at pH = 9.3 in less than 10 minutes. The applicability of the method[12] was demonstrated for forensic evidence in human's urine.
Some authors tried to use atomic absorption spectrometry (AAS)[14] or laser-excited molecular fluorescence[15] for fluoride determination in tap water, urine and some other matrices. Atomic absorption method is based on the formation of AlF radical in a graphite furnace after in situ oxygen assisted ashing of the untreated urine sample. The absorbance of this radical is measured at 227.45 nm. The authors report method as relatively easy and with low detection limit. Graphite furnace AAS suffers from strong interferences and requires good background correction system for the analysis of biological samples with complex matrix and intensive source of radiation. The other study[15] presents fluorine determination in urine using laser-excited molecular fluorescence with an unmodified atomic absorption graphite tube furnace. Molecular fluorescence from magnesium fluoride (excited at 268.94 nm, detected at 358.82 nm) was determined. The linear dynamic range of the technique was five orders of magnitude. Significant interferences arising from $Na^+$, $H^+$ and $Cl^-$ ions were observed.

## Materials and methods

We have used fluoride selective electrode Crytur 09-17 (Monokrystaly Ltd., Czech Republic) together with silver chloride reference electrode RAE 113 (Monokrystaly Ltd., Czech Republic). The selectivity coefficient of fluoride electrode introduced by the manufacturer is for $OH^-$ ions 0.1. The electrodes were connected to inoLab pH Level 1 (WTW, Germany) potentiometer. The determination of density of urine samples has been carried out with the submersible densimeter with range 1000-1060 $kg.m^{-3}$ (Exatherm Ltd., Czech Republic).
Urine samples were stored in plastic tubes before the analysis. Fluoride standard solutions ($10^{-2}$ $mol.l^{-1}$ – $10^{-6}$ $mol.l^{-1}$) were prepared by dilution of Certified Reference Material – water calibration solution with 1.000 ± 0.002 $g.l^{-1}$ (Analytika Ltd., Czech Republic) of fluoride by demineralised water (Elga system, Great Britain). A citrate buffer solutions of pH = 5.0, 5.4 and 6.0 were prepared from citric acid (p.a., Lachema, Czech Republic) and $Na_2HPO_4$ (p.a., Lachema, Czech Republic)[16]. Total Ion Strength Adjustment Buffer – TISAB (Theta 90, Czech Republic) and citrate buffer with $10^{-3}$

mol.l$^{-1}$ NaCl (p.a., Lachema, Czech Republic) were also used as solutions to adjust pH and ionic strength.
All samples and calibration standards were diluted with buffer solution (usually TISAB) 1:5 before the fluoride determination. The urine fluoride concentration depends on the liquid intake and fluid excretion from the human body (drinking regimen). The determination of creatinine or density and mathematical correction is usually used to eliminate this influence. Urine density correction has been applied before statistical treatment of the results presented in this work.
The statistical evaluation of calibration, all paired t-tests and ANOVA has been performed by QC Expert 2.5 (Trilobyte, Czech Republic) software at $\alpha = 0.05$. The median and its confidence interval have been calculated as the estimation for all fluoride concentrations shown in this work. The used statistical software uses nonparametric estimation of median's confidence interval[17] which can lead to the asymmetrical interval.

**Results and discussion**

In this work the within laboratory optimization of the method of fluoride determination in urine samples is presented. We have tested suitability of linear calibration, estimated limit of detection and quantification, accuracy and precision of the method. The accuracy has been tested using spike recovery approach. We have used 3 additions (spikes) to 5 samples and established average recovery 98.4 %. Relative standard deviation (RSD) obtained from 10 measurements during one day has been 2.8 %.
Within our one year work we came to the conclusion that calibration curve is always linear in range $10^{-2}$ – $10^{-5}$ mol.l$^{-1}$. Using lower concentration than $10^{-5}$ mol.l$^{-1}$ can sometimes lead to quadratic calibration curve. The curvature of the calibration curve is not limiting factor at all, when responsible statistical evaluation is applied. The values of mean error of prediction and Akaike information criterion have been used to choose between linear and quadratic calibration curve during routine analysis. During the period of work the slope of the linear calibration curve has been between 55 and 58 mV.pF$^{-1}$, which is very close to Nernstian calibration slope. Limits of detection and quantification were evaluated from calibration curve using direct signal method[18] after testing the suitability of calibration. For the estimation of detection and quantification limits the direct signal method was preferred to usually used "$3\times s_{blank}$" method because this method is more reliable, comes out from the tested regression (calibration) model and is recommended by IUPAC. The evaluated value of limit of detection has been $3.2.10^{-6}$ mol.l$^{-1}$ and limit of quantification $4.2.10^{-6}$ mol.l$^{-1}$.
As shown above we have tested three different buffer solutions TISAB and two ones described in literature[19]: citrate buffer with pH = 6.0 and citrate buffer with NaCl. To compare the difference between buffers one-way ANOVA method has been performed. The analysis of seven urine samples has been done with all three buffers. Statistically evaluated level (from ANOVA) of p-value = 0.057 leads to statistically insignificant differences between used buffers. In the same way the comparison of citrate buffers with pH = 5.0, 5.4, 6.0 has been carried out. Using seven samples with fluoride concentration

in range from $2.6.10^{-5}$ to $4.5.10^{-5}$ mol.l$^{-1}$ provided the same results, there is no statistically important difference in buffer composition (p-value = 0.126). The commercially available buffer TISAB is according to our experiences the most convenient one, but citrate buffer with the appropriate pH can substitute TISAB for the urine samples. On the other site it is necessary to use some buffer solution to adjust pH and eliminate the influence of the interfering ions. When we analyzed urine samples without any buffer, there was found only 69 % of fluoride concentration in comparison to the analysis with TISAB.

We tried to store urine samples at + 4 °C to prevent the formation of the sediment. The paired test has been used to compare fluoride concentrations in eight fresh samples and same samples after 10 days storage at + 4 °C and lead to the conclusion that fluoride concentration decreases (p-value = 0.006). We have tested the stability of the fluoride concentration in samples stored at – 20 °C during one, five, ten and fifteen weeks. The results of evaluation of paired t-tests have provided p-value > 0.05. From these results the conclusion that samples should be preferably stored frozen at – 20 °C can be drawn. The possible influence of the formation of the sediment in frozen samples is negligible. Sometimes heating samples in water bath at about 60 °C can dissolve the sediment.

## Conclusion

We have done within laboratory validation of the potentiometric method of fluoride determination in urine samples in limited range of parameters. The described method has good accuracy and precision and can be used to quantify fluoride in urine from $4.2.10^{-6}$ mol.l$^{-1}$ (limit of quantification). This method can be easily applied in clinical laboratory or in dentist practice if they have skilful laboratory technician. When it is not possible to analyze fresh samples, it is useful to store them at – 20 °C.

The average concentration (shown as median) in about 150 urine samples from children is $3.32.10^{-5}$ mol.l$^{-1}$ (i.e. 0.63 mg.l$^{-1}$) with its confidence interval from $2.95.10^{-5}$ to $3.58.10^{-5}$ mol.l$^{-1}$. Found concentrations are in agreement with other works[19,20]. According to the study[6] the mean urine fluoride concentrations (Table 1) with regard to the age have been calculated and the statistical analysis has been performed. The result of nonparametric Kruskal-Wallis test shows that the fluoride concentrations in three tested groups do not differ significantly (calculated $\chi^2 = 4.59$ and critical value of $\chi^2$ distribution was 5.59).

Table 1: Mean urinary fluoride concentration (mol.l$^{-1}$) according to age.

| Age group | Arithmetic mean | Median |
|---|---|---|
| Up to 5 years | $5.23.10^{-5}$ | $4.72.10^{-5}$ |
| 5-9 years | $3.95.10^{-5}$ | $3.01.10^{-5}$ |
| 10-14 years | $2.57.10^{-5}$ | $2.87.10^{-5}$ |

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## References

1. Konieczka P., Zygmunt B., Namiesnik J.: *Bull. Environ. Contam. Toxicol.* **64**, 794 (2000).
2. Itai K., Tsunoda H.: *Clin. Chim. Acta* **308**, 163 (2001).
3. Vickery B, Vickery ML: *Analyst* **101**, 445 (1976).
4. Spěváčková V., Knotková J.: *Chem. Listy* **92**, 287 (1998).
5. Frenzel W., Brätter P.: *Anal. Chim. Acta* **187**, 1 (1986).
6. Frenzel W., Brätter P.: *Anal. Chim. Acta* **188**, 151 (1986).
7. Song Z.H., Zhang N.: *Spectrosc. Lett.* **36**, 117 (2003).
8. Malát M.: *Absorpční anorganická fotometrie*. Academia, Praha 1973.
9. CSN 830520. Czech Standards Institute, Praha 1977.
10. Kuo H.W., Chang W.G., Huang Y.S., Lai J.S.: *Bull. Environ. Contam. Toxicol.* **62**, 677 (1999).
11. Michigami Y., Kuroda Y., Ueda K., Yamoto Y.: *Anal. Chim. Acta* **274**, 299 (1993).
12. Park S.W., Jin K.M., You J.H., Kim T.J., Paeng K.J., Kong K.H.: *Anal. Sci.* **13**, 243 (1997).
13. Bhemrevboom M.M.: *J. Chromatogr. A* **680**, 675 (1994).
14. Cobo G., Gomez M., Camara C., Palacios M.A.: *Mikrochim. Acta* **110**, 103 (1993).
15. Butcher D.J., Irwin R.L., Takahashi J., Michel R.G.: *J. Anal. Atom. Spectrom.* **6**, 9 (1991).
16. Sýkora V.: *Chemickoanalytické tabulky*. SNTL, Praha 1976.
17. Kupka K.: *Statistické řízení jakosti*. Trilobyte Ltd., Pardubice 1997.
18. Meloun M., Militký J.: *Statistické zpracování experimentálních dat*. Plus, Praha 1994.
19. Broukal Z., Ryšavá L., Zajíček O., Dušková J., Mrklas L.: *Čes. Stomatol*. **102**, 229 (2002).
20. Heintze S.D., Bastos J.R.D., Bastos R.: *Community Dent. Oral Epidemiol*. **26**, 316 (1998).

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# SIX NEW Ni(II) DITHIOCARBAMATES DERIVED FROM HEXAMETHYLENEIMINE WITH TRIPHENYLPHOSPHINE OR TRIBUTYLPHOSPHINE AS π-ACCEPTOR LIGANDS

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**Abstract**

Six novel heterocyclic Ni(II) dithiocarbamates with $NiS_2P_2$ chromophores of composition $[Ni(hmidtc)(PR_3)_2]X$ (hmi = $C_6H_{12}$; dtc = $S_2CN^-$; R = phenyl, butyl; X = $ClO_4$, $PF_6$, $BPh_4$ (Ph = phenyl) have been prepared. These compounds have been studied by elemental analyses, IR and electron spectroscopy, magnetochemical and conductivity measurements and thermal analysis. These used methods indicate that the complexes are mononuclear square-planar heterocyclic dithiocarbamates with triphenylphosphine or tributylphosphine in the coordination sphere.

**Key Words:** *nickel(II) dithiocarbamates, phosphines, synthesis, physico-chemical study*

## Introduction

Group VIII dithiolates of $MS_4$ chromophore react with Lewis bases to give adducts or substitution products. In the case of nickel dithiocarbamates, $Ni(dtc)_2$ (dtc = differently substituted dithiocarbamate anions), exhibit an interesting intermediate reactivity towards Lewis bases compared to highly reactive xanthates and just about inert 1,2-dithiolates[1]. Nickel(II) dithiocarbamates in which one of the dtc anions is replaced by a monodentate or bidentate P-donor ligand were studied most extensively. Pavlíček *et al.*[2] prepared and structurally characterized Ni(II) dithiocarbamates of the composition

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[NiX(hmidtc)Y]·$n$CHCl$_3$ (X = Cl, Br, I or NCS; hmi = $C_6H_{12}$; dtc = $S_2CN^-$; Y = $PPh_3$ = triphenylphosphine or $PBu_3$ = tributylphosphine; $n$ = 0, 1). These complexes are diamagnetic with square-planar arrangement about the central atom with $NiS_2PX$ chromophore. Mixed ligand Ni(II) dithiocarbamates derived from morpholine or hexamethyleneimine of the type [Ni$_2$(μ-dpph)(hmidtc)$_2$X$_2$] (where X = Cl, Br, I, $ClO_4$ or NCS; dpph = 1,6-bis(diphenylphosphino)hexane) and [Ni(morphdtc)(P,P)]X or [Ni$_2$(μ-P,P)(morphdtc)$_2$X$_2$] (X = NCS, $ClO_4$, I; P,P = 1,2-bis(diphenylphosphino)ethane (dppe); 1,4-bis(diphenylphosphino)butane (dppb); 1,6-bis(diphenylphosphino)hexane (dpph), 1,1´-bis(diphenylphosphino)ferrocene (dppf); morph = $C_4H_8O$) have been also prepared by Pastorek *et al.*[3-4]. X-ray structural analysis was solved for the [Ni$_2$(μ-dpph)(hmidtc)$_2$Br$_2$]·2CHCl$_3$, [Ni(morphdtc)(dppf)]$ClO_4$·$C_2H_5OH$ and confirmed the presence of two $NiS_2PBr$ chromophores (for binuclear complex) and $NiS_2P_2$ chromophore (for mononuclear complex). Nickel(II) piperidinedithiocarbamates of the general formula [Ni(pipdtc)(P,P)]X, [Ni$_2$(μ-dpph)(pipdtc)$_2$(NCS)$_2$] (X = NCS, $ClO_4$, I; P,P = dppe, dppb, dpph, dppf; pip = $C_5H_{10}$) have been synthetized and structurally characterized[5]. These prepared complexes were characterized as binuclear or mononuclear nickel(II) diamagnetic non-electrolytes or electrolytes (1:1), respectively, with the polydentate phosphorus donor ligands in the coordination sphere of the central atom. Akilan *et al.*[6] structurally characterized Ni(II) dithiocarbamate derived from morpholine. The X-ray analysis of [Ni(morphdtc)(dppe)]$ClO_4$·$CH_2Cl_2$ verified square-planar arrangement about the nickel atom with $NiS_2P_2$ chromophore. Very similar dithiocarbamates with the bidentate P-donor ligands in the coordination sphere of the composition [Ni(Rdtc)(P,P)]X·$n$H$_2$O, [Ni$_2$(μ-dppb)(plddtc)$_2$(NCS)$_2$]·2H$_2$O or [NiX(plddtc)($PPh_3$)]·0,5CHCl$_3$ (where X = Cl, Br, I, $NO_3$, $ClO_4$; R = pld = $C_4H_8$, tz = $C_3H_6S$; P,P = dppe, dppb, dpph; $n$ = 1, 2) were prepared and structurally characterized by Pastorek *et al.*[7-9] The central atoms are four-coordinated in a distorted square-planar arrangement.

Our aim was to isolate and to characterize of the new nickel hexamethyleneimine dithiocarbamate complexes of bivalent nickel with triphenylphosphine or tributylphosphine in the coordination sphere.

## Materials and methods

*Materials*

Triphenylphosphine, tributylphosphine, sodium tetraphenylborate and potassium hexafluorophosphate were supplied by Fluka Co.; lithium perchlorate trihydrate was obtained from Aldrich Co.; nickel(II) chloride hexahydrate and other chemicals were obtained from Lachema Co. All chemicals were of p.a. purity.

*Preparation of [Ni(hmidtc)($PPh_3$)$_2$]$ClO_4$* **(1)**

To a suspension of [NiCl(hmidtc)($PPh_3$)]·CHCl$_3$ (ref.[2]) (1 mmol) in $CH_3OH$ (25 cm$^3$) the mixture of $PPh_3$ (1 mmol) and $LiClO_4$·3H$_2$O (1 mmol) was added. The reaction mixture was stirred under reflux untill all components were dissolved. After 3 h red solution was filtered. Red microcrystals, that were formed after 2 days, were filtered off,

washed by $Et_2O$ (2 × 10 $cm^3$) and dried under IR lamp at 40 °C. The microcrystalic product was recrystalized from $CH_3OH$. Yield: 26%.

*Preparation of [Ni(hmidtc)(PPh$_3$)$_2$]PF$_6$* **(2)**

To a solution of [NiCl(hmidtc)($PPh_3$)]·$CHCl_3$ (1 mmol) in $CHCl_3$ (20 $cm^3$) the solution of $PPh_3$ (1 mmol) in acetone (5 $cm^3$) and $KPF_6$ (1 mmol) in acetone (10 $cm^3$) was added. The reaction mixture was stirred under reflux for 4 h. Red solution was filtered off. 20 $cm^3$ of $Et_2O$ was added to the oily product after 3 days. Pink-red powder was filtered off, washed by $Et_2O$ (2 × 10 $cm^3$) and dried under IR lamp at 40 °C. The powdered product was recrystalized from $CHCl_3$. Yield: 36%.

*Preparation of [Ni(hmidtc)(PPh$_3$)$_2$]BPh$_4$* **(3)**

To a suspension of [NiCl(hmidtc)($PPh_3$)]·$CHCl_3$ (1 mmol) in $CH_3OH$ (25 $cm^3$) the mixture of $PPh_3$ (1 mmol) and $NaBPh_4$ (1 mmol) was added. The reaction mixture was stirred under reflux untill all components were dissolved. The product of the reaction was observed after 3 h. Orange powder was filtered off, washed by $Et_2O$ (2 × 10 $cm^3$) and dried under IR lamp at 40 °C. The powdered product was recrystalized from $CH_3OH$. Yield: 63%.

*Preparation of [Ni(hmidtc)(PBu$_3$)$_2$]ClO$_4$* **(4)**

Finely powdered [NiI(hmidtc)($PBu_3$)] (ref.[2]) (1 mmol) was added to a solution of $LiClO_4·3H_2O$ (1 mmol) in $CH_3OH$ (25 $cm^3$), then the reaction mixture was stirred at room temperature for 5 min. To the resulting mixture $PBu_3$ (1 mmol) was added. The solution was stirred under Ar and heated under reflux for 3 h. The resulting red solution was filtered. Red microcrystals, that were formed after 7 days, were filtered off, washed by $Et_2O$ (2 × 10 $cm^3$) and dried in vacuum desiccator. Yield: 35%.

*Preparation of [Ni(hmidtc)(PBu$_3$)$_2$]PF$_6$* **(5)**

To a suspension of [NiI(hmidtc)($PBu_3$)] (1 mmol) in $CH_3OH$ (25 $cm^3$) the solution of $KPF_6$ (1 mmol) in acetone (5 $cm^3$) and $PBu_3$ (1 mmol) was added. The reaction mixture was stirred under Ar and heated under reflux for 3 h. The resulting orange solution was filtered. Orange powder, that were formed after 3 days, were filtered off, washed by $Et_2O$ (2 × 10 $cm^3$) and dried in vacuum desiccator. Yield: 45%.

*Preparation of [Ni(hmidtc)(PBu$_3$)$_2$]BPh$_4$* **(6)**

To a suspension of [NiI(hmidtc)($PBu_3$)] (1 mmol) and $NaBPh_4$ (1 mmol) in $CH_3OH$ (25 $cm^3$) $PBu_3$ (1 mmol) was added. The reaction mixture was stirred under Ar and heated under reflux for 3 h. The resulting solution was filtered into $Et_2O$ (5 $cm^3$). Red microcrystals, which formed after 4 days, were filtered off, washed by $Et_2O$ (2 × 10 $cm^3$) and dried in vacuum desiccator. Yield: 25%.

*Physical measurements*

The carbon, hydrogen, nitrogen and sulphur analyses were performed on an EA1108 instrument (Fisons). The content of nickel was estimated by the chelatometric titration after dissolving of sample in $HNO_3$ with murexide as an indicator[10] while

chlorine was determined according to Schöniger´s method[11]. IR spectra were recorded on a Specord M 80 (Carl Zeiss, Jena) spectrophotometer, electron diffuse-reflectance spectra were recorded on a Specord M 40 (Carl Zeiss, Jena) instrument with samples in Nujol mulls. Magnetochemical data were obtained at 296 K using the Faraday´s method. $Hg[Co(SCN)_4]$ was used as a calibrant. The thermal study was carried out on derivatograph Q-1500 (MOM, Budapest) using static air atmosphere with sample weight about 150 mg and thermal gradient 5 °C/min. The molar conductivities were measured on Conductivity Meter LF 340 (WTW, Germany) at 25 °C in nitromethane solutions (c = $10^{-3}$ mol/dm$^3$).

## Results and discussion

The reaction between the starting nickel(II) dithiocarbamate $[NiCl(hmidtc)(PPh_3)]\cdot CHCl_3$ and monodentate P-donor ligand (triphenylphosphine or tributylphosphine) in presence of perchlorate, tetraphenylborate or hexafluorophosphate ion in $CH_3OH$ or $CHCl_3$ (molar ratio 1:1:1) gave complexes of the composition $[Ni(hmidtc)(PPh_3)_2]X$ or $[Ni(hmidtc)(PBu_3)_2]X$, where hmidtc = hexamethyleneiminedithiocarbamate, $PPh_3$ = triphenylphosphine, $PBu_3$ = tributylphosphine; X = $ClO_4$, $PF_6$, $BPh_4$. Analytical data and compositions of the prepared complexes are given in Table 1. Spectral, thermal and conductivity data are summarized in Table 2.

The complexes are stable at room temperature at air, and insoluble in most common organic solvents. All of the prepared compounds behave as electrolytes 1:1 in nitromethane solutions[12]. The molar conductivities of the complexes in nitromethane ($10^{-3}$ mol/dm$^3$) are in the region of 77.8 – 88.0 S cm$^2$ mol$^{-1}$. The results show that simple inorganic ion X are situated outside of the inner coordination sphere of the central atom. An assumption of square-planar coordination around nickel(II) atoms is supported by magnetochemical measurements (all the complexes are diamagnetic) and diffuse-reflectance spectra. Absorption maxima observed in the electronic spectra of the complexes in the region 15400 - 16600 cm$^{-1}$ and 18300 – 20400 cm$^{-1}$ are attributable to the following d-d transitions of square-planar nickel(II) complexes: $^1A_{1g}\rightarrow{}^1A_{2g}$ and $^1A_{1g}\rightarrow{}^1B_{1g}$, respectively[13]. The other maxima displayed in the 31200 – 33200 cm$^{-1}$ range are probably connected with the intraligand $n\rightarrow\pi^*$ transition localized on sulphur in the $S_2CN$ group[14]. The infrared spectra of all complexes were not studied in detail, only the characteristic vibrations for dithiocarbamate anion $\nu(C\cdots N)$ and $\nu(C\cdots S)$ were interpreted. The characteristic bands of $\nu(C\cdots N)$ and $\nu(C\cdots S)$ were found at 1520 - 1542 cm$^{-1}$ and 996 – 1008 cm$^{-1}$, respectively[14,15]. The complexes **(1)** and **(4)** exhibit non-split maxima $\nu_3(ClO_4)$ and $\nu_4(ClO_4)$ due to ionic character of $ClO_4$ group[16]: 1086, 620 cm$^{-1}$ for **(1)** and 1096, 620 cm$^{-1}$ for **(4)**. The bands observed in the IR spectra of complexes **(3)**, **(6)** at 3138, 1568 cm$^{-1}$ for **(3)** and 3120, 1578 cm$^{-1}$ for **(6)** are connected with $\nu(C–H)_{ar}$, and $\nu(C–C)_{ar}$[17]. The peaks appearing at 1090 cm$^{-1}$ in the IR spectra of all complexes belong probablly to the carbon-nitrogen stretch vibration of the hexamethyleneimine group[17]. Thermal analysis was studied only for **(2)**, **(3)**, **(5)**, **(6)**; the perchlorate complexes were not examined for safety reasons. Thermolysis of all prepared compounds is very similar.

$[Ni(hmidtc)(PBu_3)_2]BPh_4$ exhibits a small *endo*-effect at 90 °C (melting point 88 °C). The initial transformations of weight in the temperature range 120 – 150 °C coincide with the insertion of oxygen into the Ni–P bond (the Ni–O–P bond is formed)[18]. These conclusions are supported on the TG curves by the slight increasing of mass and on the DTA curves by a small *exo*-effect within the temperature range 128 – 162 °C. Thermal decompositions starts in the interval 150 - 210 °C and goes continuously without formation of thermally stable intermediates (no plateau on TG curve) to the 710 - 790 °C (the thermal analyses are finished). These changes are accompanied by *exo*-effects on the DTA curves: 412, 430 and 510 °C for **(2)**; 410, 540 °C for **(3)**; 335, 415, 520 and 590 °C for **(5)**; 210, 312 and 540 °C for **(6)**. The final products of the thermal analyses are not proved.

**Table 1.** Analytical data for the nickel(II) complexes

| Complex | Found (Calcd.) (%) | | | | | |
|---|---|---|---|---|---|---|
| | C | H | N | S | Ni | Cl |
| **(1)** $[Ni(hmidtc)(PPh_3)_2]ClO_4$ | 60.1(60.3) | 5.4(4.9) | 1.5(1.6) | 6.6(7.5) | 6.9(6.9) | 3.5(4.1) |
| **(2)** $[Ni(hmidtc)(PPh_3)_2]PF_6$ | 56.6(57.2) | 4.5(4.7) | 1.5(1.6) | 6.6(7.1) | 6.4(6.5) | - |
| **(3)** $[Ni(hmidtc)(PPh_3)_2]BPh_4$ | 73.5(74.7) | 5.6(5.8) | 1.9(1.3) | 4.6(6.0) | 5.4(5.5) | - |
| **(4)** $[Ni(hmidtc)(PBu_3)_2]ClO_4$ | 50.4(50.5) | 8.7(9.0) | 2.0(1.9) | 7.9(8.7) | 7.8(8.0) | 4.4(4.8) |
| **(5)** $[Ni(hmidtc)(PBu_3)_2]PF_6$ | 47.3(47.6) | 8.2(8.5) | 1.8(1.8) | 8.5(8.2) | 7.7(7.5) | - |
| **(6)** $[Ni(hmidtc)(PBu_3)_2]BPh_4$ | 68.6(69.0) | 9.0(9.1) | 1.5(1.5) | 6.6(6.7) | 6.0(6.1) | - |

**Table 2**. Colour, IR and UV/VIS spectra, thermal and conductivity data for the nickel(II) complexes

| Compd. | Colour | IR data [$cm^{-1}$] | | UV-VIS data | $T_1$[a] | $T_2$[b] | $\lambda_M$[c] |
|---|---|---|---|---|---|---|---|
| | | ν(C⎓S) | ν(C⎓N) | [$\cdot 10^3$ $cm^{-1}$] | [°C] | [°C] | [S $cm^2$ $mol^{-1}$] |
| **(1)** | red | 996 | 1520 | 16.0; 18.3; 31.2 | - | - | 77.8 |
| **(2)** | pink-red | 996 | 1532 | 16.6; 20.2; 31.4 | 205 | 790 | 87.0 |
| **(3)** | orange | 996 | 1542 | 15.4; 19.8; 31.8 | 150 | 720 | 79.2 |
| **(4)** | red | 1008 | 1530 | 16.1; 20.2; 33.2 | - | - | 86.8 |
| **(5)** | orange | 1004 | 1528 | 15.8; 20.4; 32.1 | 210 | 750 | 77.5 |
| **(6)** | red | 1004 | 1520 | 15.4; 20.2; 32.8 | 150 | 710 | 85.6 |

[a]The beginning of thermal decomposition. [b]The termination of thermal decomposition. [c]Measured in nitromethane solution ($10^{-3}$ mol/$dm^3$).

From the experimental results and from the literature informations we can derive that all of the prepared compounds are mononuclear nickel(II) species in which the metal centre has a square-planar coordination with the $NiS_2P_2$ chromophore. The monodentate phosphine (triphenylphosphine or tributylphosphine) complete the coordination sphere of the central atom (Fig. 1).

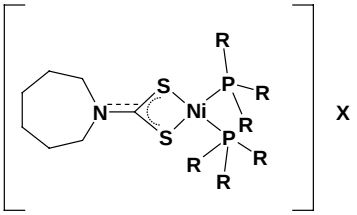


**Figure 1.** Predicted structure for the nickel(II) dithiocarbamates (R = phenyl or buthyl, X = $ClO_4$, $PF_6$, $BPh_4$)

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## References

1. Lockyer T. N. and Martin R. L.: *Prog. Inorg. Chem.*, **27**, 223 (1980).
2. Pavlíček M., Trávníček Z., Pastorek R. and Marek J.: *Transition Met. Chem,* **28**, 260 (2003).
3. Pastorek R., Kameníček J., Husárek J., Pavlíček M., Šindelář Z. and Žák Z.: *Polish J. Chem.*, **77**, 805 (2003).
4. Pastorek R., Kameníček J., Šindelář Z. and Žák Z.: *Polish J. Chem.,* **75**, 363 (2001).
5. Pastorek R., Trávníček Z., Marek J., Dastych D., Šindelář Z.: *Polyhedron*, **19**, 1713 (2000).
6. Akilan R., Sivakumar K., Venkatachalam V., Ramalingam K., Chinnakali K. and Fun H-F.: *Acta Cryst. C,* **51**, 368 (1995).
7. Pastorek R., Trávníček Z., Šindelář Z. and Březina F.: *Polyhedron,* **21**, 3691 (1996).
8. Pastorek R., Trávníček Z., Ptošek P., Šindelář Z., Březina F. and Marek J.: *J. Coord. Chem.,* **44**, 247 (1998).
9. Pastorek R., Trávníček Z., Kvapilová E., Šindelář Z., Březina F., Marek J.: *Polyhedron,* **18**, 151 (1999).
10. Přibil R.: *Komplexometrické titrace*, SNTL Praha 1955, p. 22.
11. M. Jureček, *Organická analýza II,* ČSAV Praha, 1957, p. 140.
12. Geary W. J.: *Coord. Chem. Rev.* **7**, 81 (1971).
13. Lever A. B. P.: *Inorganic Electron Spectroscopy,* Elsevier, Amsterdam 1968, p. 343.
14. Tsipis C. A., Kessissoglou D. P. and Katsoulos G. A.: *Chim. Chron., New Ser.,* **14**, 195 (1985).
15. Larionov S. V., Patrina L. A., Oglezneva I. M. and Uskov E. M.: *Koord. Chim.,* **10**, 92 (1984).
16. Scholer P., Merbach A. E.: *Inorg. Chim. Acta,* **15**, 15 (1975).
17. Pouchert C. J.: *The Aldrich Library of Infrared Spectra (Edition III),* Aldrich Chemical Co., Inc., Milwaukee, Wisconsin 1981, p. 53233.
18. Pastorek R., Kameníček J., Husárek J., Pavlíček M., Šindelář Z. and Žák Z.: *Polish J. Chem.,* **76**, 1545 (2002).

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