

To the 100th Anniversary of M.G. Voronkov

Contribution of the Scientific School of Academician M.G. Voronkov to the Development of the Chemistry of Biologically Active Atranes (Protatranes and Hydrometallatranes) (A Review)

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Abstract—The main results of the many years' studies of the scientific school of Academician Mikhail G. Voronkov in the field of two subgroups of the atrane family (protatranes and hydrometallatranes) as well as the results of research in continuation of the studies initiated by Academician M. G. Voronkov have been summarized and presented. Long-term studies of atranes under the leadership of M. G. Voronkov have led to the discovery of their unique biological activity and the creation of a series of unique original drugs and means of agricultural chemicalization: biostimulants and adaptogens for agricultural plants, animals, useful insects and microorganisms.

Keywords: atranes, protatranes, hydrometallatranes, triethanolamine, trecresan, biologically active substances

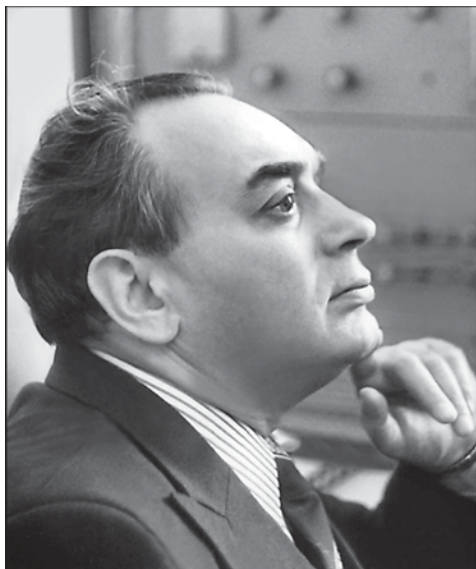
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1. INTRODUCTION

It is well known that atranes (chelate compounds of hydroxyalkylamines with organosilicon, organogermanium, organotin, and other organoelement and coordination compounds, containing a transannular donor-acceptor N→M bond) exhibit broad range of strong specific biological activity. However, biological activity of organosilicon compounds remained practically unknown until 1964, when Academician M.G. Voronkov discovered

extremely strong toxicity of 1-phenylsilatrane, which then led to the development of new-generation environmentally safe zoocides. It was that discovery which served a strong impact to the development of organosilicon chemistry and extensive study of the atranes class compounds. The studies of M.G. Voronkov in the field of atranes started in the second half of the 20th century have been well recognized by scientific community, and related research has been ongoing. Extensive investigation of biological activity of the atranes has led to the



development of a broad range of drugs: novel classes of adaptogens and immunomodulators, including trecresan (crezacin) based on tris(2-hydroxyethyl)ammonium 2-methylphenoxyacetate, chlorocrezacin [a trecresan analog, tris(2-hydroxyethyl)ammonium 2-methyl-4-chlorophenoxyacetate], mival (chloromethylsilatrane), migugene (ethoxysilatrane), etc.

This review considers in more detail the main results of many years' studies of two groups of the atranes (protatranes and hydrometallatranes) in the scientific school of M.G. Voronkov as well as the results of the studies developing the research started by Academician M.G. Voronkov. Metallatranes, in particular silatranes, the best studied representatives of atranes, will not be considered. They have been comprehensively reviewed, including biological activity and practical application, in [1–4].

2. M.G. VORONKOV, INITIATOR OF THE ATRANES STUDIES

Academician M.G. Voronkov was a cosmic-scale person, and his research of course was not limited to the discovery of the atranes. Being an outstanding world-class scientist, he founded one of the leading Russian scientific schools on the field of chemistry, performing fundamental research on the chemistry of organic compounds of tetra-, hyper-, and hypovalent silicon, germanium, and tin well as organic compounds of sulfur, phosphorus, fluorine, and iodine. Moreover, he significantly contributed to physical

organic chemistry, medicinal chemistry, pharmacology, and agrochemistry. His desire to find practical applications of the research led to the contribution in many fields of industry and agriculture.

M.G. Voronkov started his scientific career in 1954 at the Grebenshchikov Institute of Silicate Chemistry, the USSR Academy of Sciences (laboratory of Professor B.N. Dolgov, pioneer of Soviet organosilicon chemistry). Scientific interests of those outstanding scientists were then focused on the chemistry of organosilicon compounds, and the fundamental research during that period was directed to the investigation of the reactions of heterolytic dissociation of the siloxane Si–O bond involving tetracoordinate silicon atom. This bond has been recognized as the most important one in the chemistry of organosilicon compounds. The research results made the basis of the Doctoral Dissertation of M.G. Voronkov and were generalized in the “Siloxane Bond” monograph [5]. The first report on the synthesis of pentacoordinate tricyclic siloxazolidines appeared in 1961 [6]. After that discovery, M.G. Voronkov started the investigation of the pentacoordinate silicon compounds [7, 8] in the Institute of Organic Synthesis, Academy of Sciences of Latvian SSR, where he headed the Laboratory of Organoelement compounds. It was M.G. Voronkov to assign the “silatranes” name to the pentacoordinate organosilicon ethers of hydroxyalkylamines.

At the Institute of Organic Synthesis, Academy of Sciences of Latvian SSR, M.G. Voronkov developed three new research directions: silatranes chemistry [9, 10], germatranes chemistry [11], and novel reactions of elemental sulfur with organic compounds [12–14]. One of them, the reaction of sulfur with arylhaloalkanes, has been known as the Voronkov reaction. This reaction is based on the interaction of elemental sulfur with arylhaloalkanes: $\text{ArC}_n\text{H}_{2n-m-1}\text{X}_m$ ($\text{X} = \text{Cl}, \text{Br}, n \geq 1, m \geq 1$) at 180–300°C and affords diverse sulfur-containing aromatic heterocyclic systems, including thiophenes, thienothiophenes, 1,4-dithiadine, and 1,2-dithiolene-3-thione, as well as stilbene derivatives [15].

Widespread occurrence of silicon in the mineral kingdom and low (almost at the level of random inclusion) occurrence in most of living organisms had been the long-lasting reasons for skeptical opinion of the researchers about the involvement of silicon in the biological processes. In 1960s, organosilicon polymers (silicones) were intensively introduced in medicine and cosmetology, for instance, implantation surgery, which also supported

the inertness of the silicon compounds. At the same time, the study of biological activity of silicon compounds was started under the supervision of M.G. Voronkov. Compounds exhibiting unusually high specific toxicity towards warm-blooded animals were discovered among the representative of the new class of pentacoordinate silicon organic compounds called silatranes by M.G. Voronkov. Those results were reported by him at the 1st International Symposium on Organosilicon Chemistry (Prague, 1965) and were considered sensational [16]. That discovery crushed the dominating conception of biological inertness of the silicon compounds with respect to living organisms, led to reevaluation of the role of that element in living nature, and the creation of a new field at the edge of chemistry, biology, and biochemistry: bioorganosilicon chemistry [17]. Following the lectures of the leading scientists on the "Silicon and life" topic at the Nobel Symposium (Stockholm, 1977), silicon was officially recognized as the element of life [18]. The discovery of specific biological activity of 1-arylsilatranes and their analogs was a strong impact to the worldwide research on synthesis and biological activity of the compounds of that class. However, the pioneering studies in that field were started in 1970s under the supervision of M.G. Voronkov. Moreover, he put the fundamental basis of chemistry of silatranes, germatranes, and other compounds of hypervalent silicon, germanium, and tin.

In 1970 M.G. Voronkov was invited to the Irkutsk Institute of Organic Chemistry, SB, AS USSR (currently Irkutsk Institute of Chemistry, SB, RAS), which he headed for 25 years. There he continued the investigation of novel biologically active chelate compounds of the atranes class.

In early 1970s, M.G. Voronkov noticed that the conversion of biologically active organic acids into their triethanolammonium salts significantly enhanced the pharmacological effect and broadened the range of their physiological action, on top of the increase in their solubility in water and reduction of the acidity [19]. That discovery was a start of the intensive study of those compounds later called protatranes by M.G. Voronkov.

In early 2000s, M.G. Voronkov and his colleagues from the Irkutsk Institute of Chemistry, SB, RAS started the research on biological activity of hydrometallatranes, coordination compounds of hydroxyalkylamines. Even though the interaction of hydroxyalkylamines with metal salts was reported in 1970s [20–22], their biological activity remained practically unknown.

In 2003 M.G. Voronkov returned to the Institute of Silicate Chemistry, RAS and headed the Laboratory of Organosilicon Compounds and Materials. There he continues the studies of the atranes, which are still ongoing.

Many years' studies supervised by M.G. Voronkov led to the discovery of the biological activity of silatranes and other atranes representatives (protatranes, metallatranes, hydrometallatranes) and development of a series of unique drugs (trecrezan, mival, silocast, feracryl, argacryl, cyacryl, acisol, citrimin, chlorocrezacin, etc.) and means of agricultural chemicalization: biostimulants and adaptogens for agricultural plants, animals, useful insects and microorganisms. The results of these research in the field of protatranes and hydrometallatranes will be considered in more detail below.

3. ATRANES

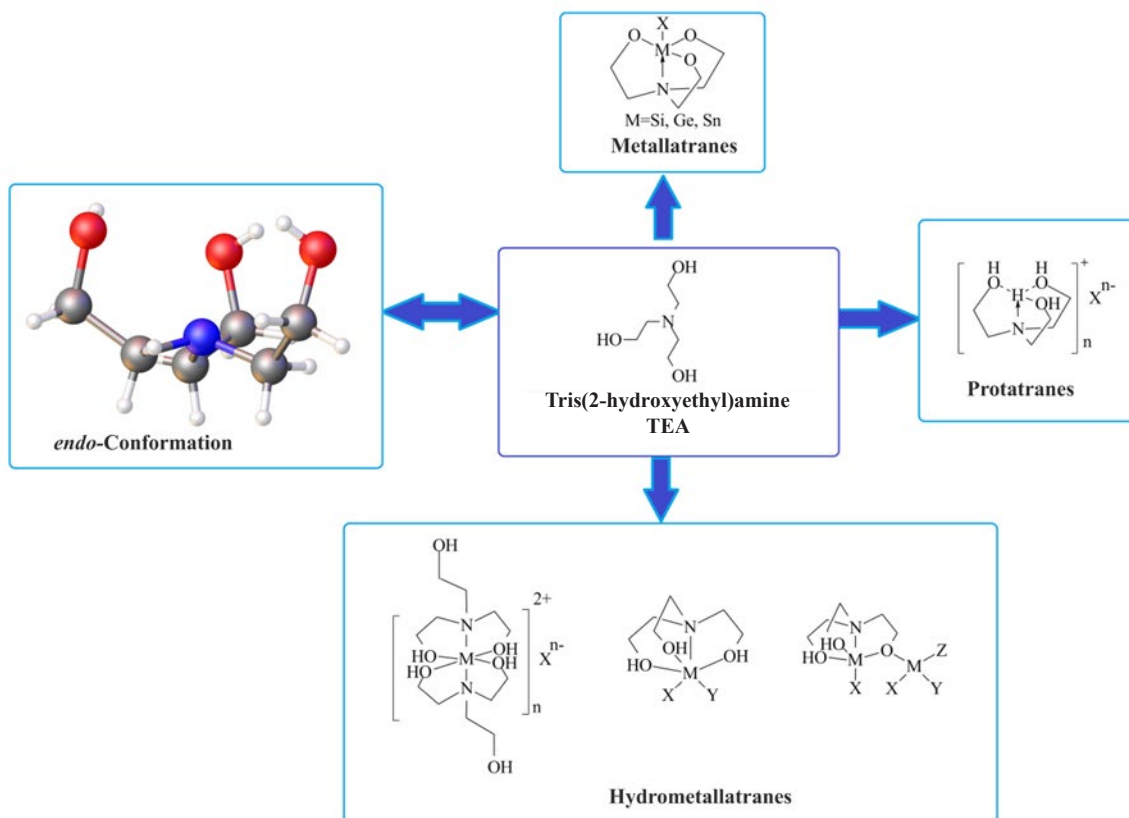
Metallatranes (silatranes, germatranes, stannatranes, etc.), protatranes (hydroxyalkylammonium salts), and hydrometallatranes (coordination compounds of hydroxyalkylamines) are commonly included in the atranes class (Scheme 1).

A metallatrane molecule is a framework construct consisting of three branches, the ends of which are converged in to three-arm nodes, forming three five-membered rings somewhat resembling a three-leaved bud. The most interesting feature of this construct is the shift of the nitrogen node atom off the plane of the three surrounding carbon atoms towards the element (Si, Ge, Sn) located in the other node, due to the formation of the transannular bond [23, 24].

High and specific biological activity of silatranes can be explained by their unusual trigonal-pyramidal structure containing the transannular donor-acceptor N→Si bond, leading to the inductive interaction between the nitrogen and oxygen atoms through the system of the σ -bonds and through the space inside the heterocyclic framework, high dipole moment of the molecule (7–10 D), and enhanced electronegativity of the endocyclic oxygen atoms, i.e. their nucleophilicity [2, 4].

It should be noted that the molecule of the parent tris(2-hydroxyethyl)amine (TEA) takes the *endo*-conformation (the lone-electron pair of nitrogen is directed inside the dome of three hydroxyethyl groups, Scheme 1), and TEA exists only in the form of dimers in the crystalline phase [25]. As expected, the *endo*-conformation of TEA is retained in the tris(2-hydroxyethyl)ammonium cations:

Scheme 1.



three hydroxyethyl branches surround the ammonium hydrogen atom with the formation of three intramolecular hydrogen bonds. Owing to this unique cation structure, tris(2-hydroxyethyl)ammonium salts and their closest structural analogs have been known as protatrane. It should be also noted that the change of the ammonium hydrogen atom to the fourth hydroxyethyl branch, in the case of the tetrakis(2-hydroxyethyl)ammonium salts $[\text{N}(\text{C}_2\text{H}_4\text{OH})_4]_n\text{X}$ leads to the disordering of the *endo*-conformation (Fig. 1) [26].

Hydrometallatrane are the products of the hydroxyalkylamines interaction with the metal salts, the complexes with transition metal salts being the most spread. Their structure can be significantly different depending on several factors, including the mononuclear cationic complexes and the polynuclear mixed-ligand ones (Scheme 1). TEA usually acts as a tri- (N,O,O') or tetradentate (N,O,O',O'') ligand in such complexes. In view of retaining of the hydroxyl hydrogen atoms and tricyclic structure of the TEA complexes,

M.G. Voronkov suggested the "hydrometallatrane" term to refer to them. However, the formation of polynuclear hydrometallatrane often results in TEA dissociation with the loss of one or several hydroxyl hydrogen atoms, and TEA can be a bridging ligand in the polynuclear complexes, linking the metal atoms (Scheme 1).

Triethanolamine N-oxide ${}^-\text{ON}^+(\text{CH}_2\text{CH}_2\text{OH})_3$ is a TEA derivative readily formed via the oxidation with hydrogen peroxide. M.G. Voronkov regarded TEA N-oxide as a parent compound of a new family of atrane, hence it was called "oxatrane" [27]. It has been suggested that oxatrane, like TEA, should take the *endo*-conformation. However, investigation of its molecular and crystal structure has revealed that three oxygen atoms of the hydroxyl groups are located practically in the plane of the carbon atoms, the NCCO torsion angles being -166° (Fig. 2a). The structure of TEA complex with oxatrane (Fig. 2b) has been studied in [28]. In this complex, TEA retains its tricyclic *endo*-conformation, forming three hydrogen bonds with the oxygen atom

of oxatrane ($\text{O}-\text{H}\cdots\text{O}_\text{N}$). The conformation of TEA N-oxide in the complex has been significantly changed in comparison with the starting oxatrane. The oxygen atoms of the hydroxyethyl groups have moved off the plane of the carbon atoms, the NCCO torsion angles being -83° (Fig. 2).

4. PROTATRANES

The study of protatranes was initiated by M.G. Voronkov et al. in early 1970s at the Irkutsk institute of Organic Chemistry, Siberian Branch, AS USSR, in order to enhance the biological activity of synthetic phytohormones such as arylheteroacetic acids. Protatranes combine the hydroxyalkylammonium cation and the X^- anion. Classical and the best studied protatranes are tris(2-hydroxyethyl)ammonium salts of protic acids. The crystal structure of the first protatrane, tris(2-hydroxyethyl) ammonium 2-methylphenoxyacetate, was elucidated by means of the X-ray diffraction analysis in 1981 [29]; that compound later was recognized as trecresan drug (known as crezacin in agriculture). The trecresan cation in the crystal takes the *endo*-conformation, in which the hydrogen atom in the N–H group was linked to

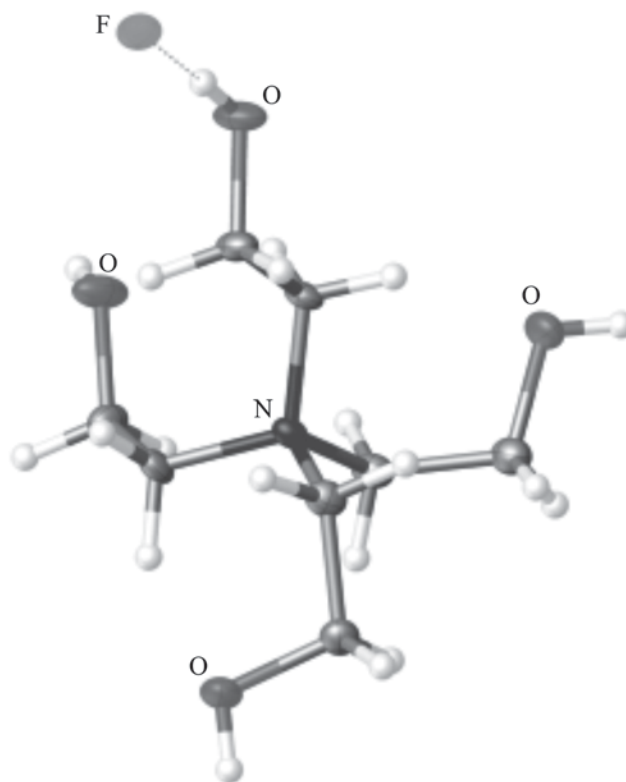


Fig. 1. Conformation of the cation in tetrakis(2-hydroxyethyl)-ammonium fluoride.

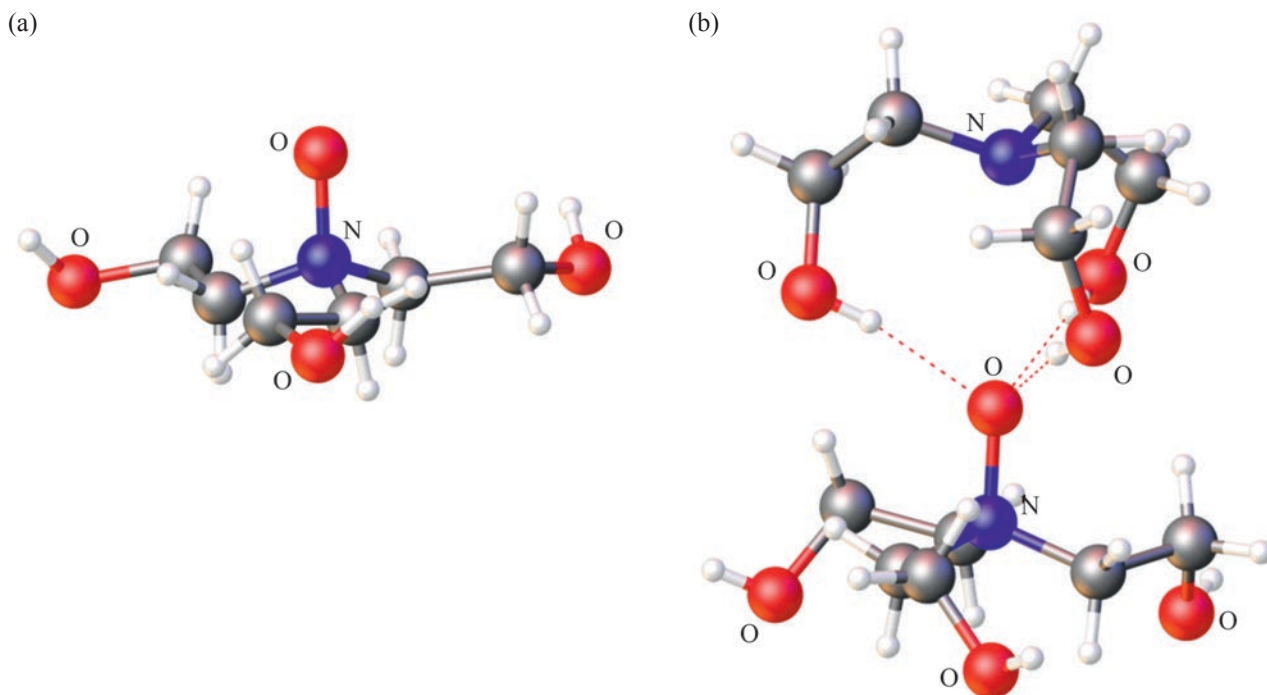


Fig. 2. Molecular structure of oxatrane (a) [27] and its complex with TEA (b) [28].

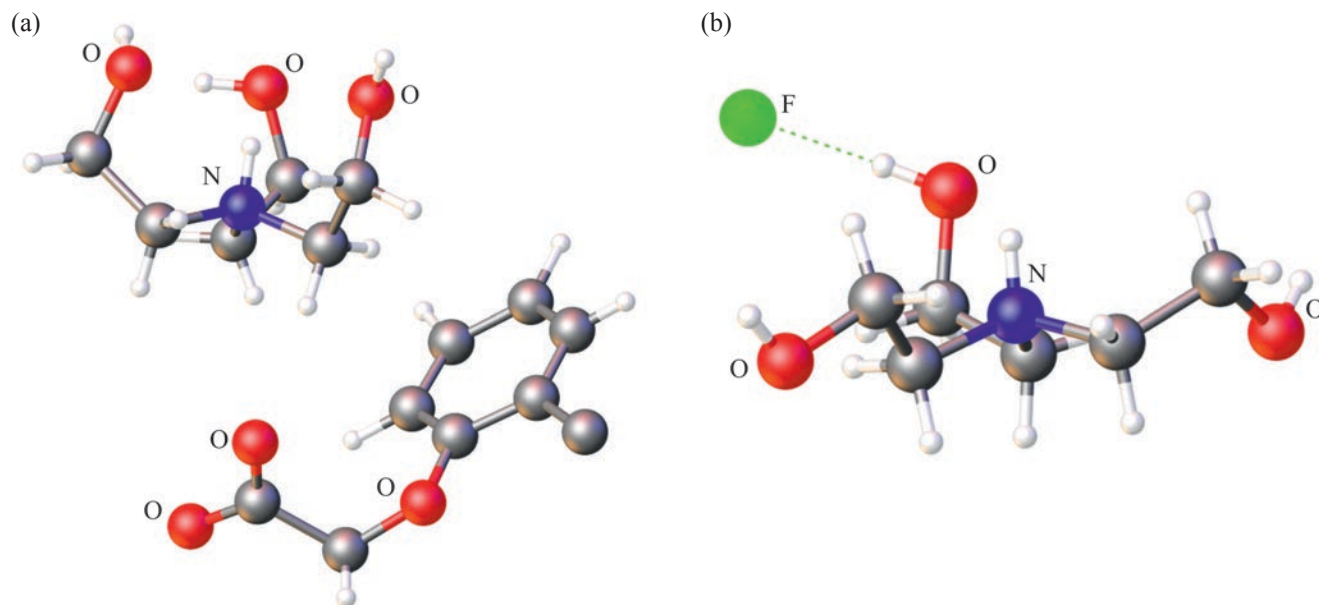


Fig. 3. Molecular structure of tris(2-hydroxyethyl)ammonium 2-methylphenoxyacetate (a) [29] and tris(2-hydroxyethyl)ammonium fluoride (b) [32].

three oxygen atoms of the $\text{CH}_2\text{CH}_2\text{OH}$ groups via the trifurcated hydrogen bond (Fig. 3a) [4].

Tris(2-hydroxyethyl)ammonium salts are readily formed via the interaction of equimolar amounts of TEA and protic acids, usually in an alcoholic or aqueous medium. The interaction of TEA with protic acids is accompanied by the acid dissociation and the proton transfer to the nitrogen atom of TEA with the formation of the tris(2-hydroxyethyl)ammonium cations $[\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_3]^+$ and the protic acid anions X^{n-} . M.G. Voronkov et al. have elaborated an original method for the synthesis of tris(2-hydroxyethyl)ammonium salts of inorganic acids $[\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_3]\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4$, etc.), based on the interaction of TEA with the corresponding ammonium salts NH_4X in aqueous or nonaqueous medium as well as in bulk [30].

The quantum-chemical simulation has revealed [31] that the interaction of TEA with the acids HX leads to the formation of two types of the $[(\text{HOCH}_2\text{CH}_2)_3\text{NH}]^+\cdots\text{X}$ complexes: the hydrogen-bound ones, with the $\text{N}\cdots\text{H}$ interatomic distance of 1.5 Å and the charge-transfer ones with the N^+-H covalent bond length of 1.0 Å.

Tricyclic *endo*-conformation of the cation is typical of most of the tris(2-hydroxyethyl)ammonium salts. However, tris(2-hydroxyethyl)ammonium fluoride [32] is characterized by an unusual conformation, which is strongly different from conventional tricyclic one.

As in the case of oxatrane, two hydroxyethyl branches are in the plane of the carbon atoms, whereas the third branch is off the plane, being directed towards the ammonium hydrogen atom (*endo*-branch) (Fig. 3b). The intramolecular distances between the nitrogen atom and three oxygen atoms are strongly different. This fact points at the asymmetry of the protatrane skeleton and, hence, inductive interaction of the nitrogen atom with only a single oxygen atom of the hydroxyethyl group.

The study of the protatranes structure has been followed by the investigation of their biological activity. Tris(2-hydroxyethyl)ammonium 2-methylphenoxyacetate (trecresan, crezacin) is the most studied protatrane in this regard. Its high biological activity is due to the combination of the acetoxyacetic acid anion and the tris(2-hydroxyethyl)ammonium cation fragments in the structure. Trecresan has been approved as a new immunomodulator and adaptogen by the Ministry of Health of Russia [33].

Long-term comprehensive studies of trecresan at the Irkutsk Institute of Chemistry, SB, RAS in collaboration with several biological and medical research institutes have revealed that regarding the range of physiological action trecresan is similar to natural adaptogens (ginseng, eleuthero, golden root, etc.), however its efficiency is significantly higher [34]. Trecresan is a low-toxic compound (LD_{50} for rats > 3700 mg/kg in the case of

intraperitoneal administration and > 6300 mg/kg in the case of peroral one, for mice > 2000 mg/kg in the case of intraperitoneal administration and > 3200 mg/kg in the case of peroral one) [35]. It enhances the cytokine activity of the total tryptophanyl-mRNA synthase via stimulation of the synthesis of specific matrix RNA-synthase. This is a key stage in the complex mechanism of the drug action [36, 37]. Trecrezan exhibits the stress-protective action in the models of immobilization and pain hypodynamic stress, can accelerate the damaged tissues (liver, myocardium, and muscles) reparation, and protects the internals from the damaging action of toxins, microwave irradiation, and infections. It possesses a unique combination of antioxidant, antihypoxic, reparative, antitoxic, adaptogen, immunostimulating, hemostimulating, antiinflammatory, cholagogic, gonadotropic, and antitumoral properties [35, 38]. Trecrezan stimulates the secretion of α - and γ -interferons and favors the improvement and correction of an organism immune status via the activation of cellular and humoral immune systems; hence, it should be regarded as a highly efficient immunomodulator. The enhancement of the immunomodulating activity of trecrezan in combination with other immunomodulators can achieve better therapeutic results in the treatment of primary and secondary immunodeficiencies [39, 40]. Trecrezan is also efficient under extremal climatic and geographical conditions, during overwork in physical and mental activity, in sport, during viral catarrhal illnesses, heavy infections, and the diseases associated with the decrease in immunity. It is applicable in the prevention of oncological diseases and in the correction of the psychoemotional status of narcological patients [34]. Trecrezan is also efficient in the complex treatment of tuberculosis and can be used in the case of heavy somatic pathology [41]. Trecrezan can be used as an efficient drug in the complex system of the methods for the prevention and treatment of coronavirus infection aftereffects, including these related to bronchopulmonary pathology [42].

Trecrezan (crezacin) has been used in agriculture as a regulator of productivity and adaptive properties of plants as well as for the enhancement of reproductive performance and productivity of animals, birds, and useful insects [41, 43, 44]. Crezacin has a multifunctional action on plants: it accelerates the seeds germination, increases the plants height, top and roots mass, productive bushiness, and ear mass, favors the formation of larger corn seeds, and improves the resistance of plants to

negative environmental factors and diseases [45]. Low damaging temperature stimulates the decomposition of inhibitors of peroxide oxidation of lipids; hence the phospholipid base of the membranes is decomposed and their functional activity is suppressed, which leads to the cells death [46]. The mechanism of crezacin action consists in the membrane-stabilizing effect and the increase in the content of vitamins A and E in the membranes, which decelerate the peroxide oxidation of lipids [47, 48].

Tris(2-hydroxyethyl)ammonium 2-methyl-4-chlorophenoxyacetate is the closest analog of trecrezan and is widely known as chlorocrezacin. Like trecrezan, chlorocrezacin exhibits adaptogen, haemopoiesis- and immunomodulating properties [41, 49, 50]. Chlorocrezacin is the most efficient in the enhancement of an organism resistance during cytotoxic hypoxia, hyper- and hypothermia, and the impact of toxic compounds [51] and electromagnetic radiation [52], being harmless. Chlorocrezacin prevents the neural activity disorders under the impact of microwave irradiation. Antioxidant activity can be regarded among possible mechanisms of protective action of chlorocrezacin [53].

Chlorocrezacin suppresses the growth of adenocarcinoma 755 (93–97%) and large intestine carcinoma (33%), reliably suppresses proliferation of tumor cells of mastocytoma R815, melanoma V16, lymphoma L1210, and hepatoma G27, and decelerates the dissemination of hepatoma G27 in lungs and melanoma V16. Its protective activity and efficiency exceed these of a known antitumor drug 5-fluorouracil [54]. Chlorocrezacin can enhance the resistance of the vascular system to cholesterol during atherosclerotic process [55].

Administration of chlorocrezacin significantly enhances the expression of matrix RNA of tryptophanyl-tRNA-synthase (by 60% in the 15 mg/kg dose). It should be noted that trecrezan increases the activity of TRSase by only 20% in comparison with the control in the dose almost twice higher (25 mg/kg) than that of chlorocrezacin [56]. Chlorocrezacin is more efficient than trecrezan in the inhibition of thrombocytes aggregation, it improves the antithrombotic properties of the vascular cells, decelerates peroxide oxidation of lipids, and enhances the tolerance of the blood cells to the action of disintegrating agents [57].

Hydroxyalkylammonium salts of sulfur-containing acids, being low-toxic (LD_{50} 1300–6000 mg/kg), also exhibit strong and diverse biological activity (hemo- and immunotropic, cardiotropic, antiinflammatory,

antithrombotic, antioxidant, adaptogen, hypocholesteremic, etc.) and are highly efficient growth-promoting preparations for the use in biotechnology processes [58, 59]. Biological activity of hydroxyalkylammonium salts of sulfur-containing acids often exceeds that of the related alkylammonium salts of aroxyacetic acids. Their activity is enhanced with the increase in the oxidation degree of sulfur and depends on the structure of the hydroxyalkylammonium fragment [60, 61]. Two salts are the most remarkable: tris(2-hydroxyethyl)ammonium indol-3-yl- and 1-benzylindol-3-ylsulfanylacetate (indacetamin and vilim, respectively). Indacetamin exhibits a wide range of biological activity: it is an efficient antiaggregant, stabilizer of cell membrane of erythrocytes and thrombocytes, antioxidant, and protector against ultrasonic and γ -irradiation [62–67].

A distinct feature of indacetamin [68, 69] and vilim [70, 71] is the pronounced antiproliferative activity in the culture *in vitro* and immunodepressive properties *in vivo* at relatively low toxicity. Vilim is an immunodepressant with antitumor activity. It should also be noted that indacetamin and vilim can selectively affect the relative activity of the T- and B-system of immunity, resulting in the deviation of the immune response in the desired (Th1 or Th2) direction [62].

Tris(2-hydroxyethyl)ammonium 4-chlorophenylsulfanylacetate (sulfacetamin) is low-toxic (LD_{50} 6000 mg/kg) and exhibits high physiological activity in the micro concentration (10^{-5} – 10^{-8} mol/L), namely growth-promoting action in the culturing of useful bacteria, bakery yeast, production of food citric acid, fungi, and in the sprouting of barley for the production of brewer's malt [58].

Liquid water-soluble derivatives of aspirin based on 2-hydroxyethylammonium salts of *O*-acetylsalicylic acid, suitable for intravenous administration and exhibiting antiinflammatory activity have been obtained in [72]. The antiinflammatory activity has been found the highest in the case of tris(2-hydroxyethyl)ammonium *O*-acetylsalicylate.

In one of the last papers, M.G. Voronkov et al. [73] have reported the synthesis of potentially biologically active aroxyprotatranes obtained via the interaction of TEA and other hydroxyalkylamines with phenol as well as 2-, 2,4-di-, and 2,4,6-trinitrophenols. Being strong acids, nitrophenols form the proton-transfer complexes with TEA, containing the onium nitrogen atom (N^+-H).

The study of protatranes are currently ongoing at the Irkutsk Institute of Chemistry, SB, RAS as well as at the Grebenshchikov Institute of Silicate Chemistry, RAS. At the Irkutsk Institute of Chemistry, SB, RAS, synthesis of novel representatives of protatranes and their biological activity are investigated. For example, recent papers by S.N. Adamovich et al. have revealed that protatranes are:

—potential biostimulants of growth of listeria and staphylococcus (*L. monocytogenes*, *S. aureus*); the use of protatranes accelerates the culturing of aurococcus for the diagnostics of infections, reducing the culturing from 48 to 6–9 h in comparison with the standard nutrient medium [74–76];

—potential biostimulants of growth of the *Saccharomyces cerevisiae* (concentration 10^{-4} – 10^{-8} wt %) and *Candida ethanolica* (10^{-6} – 10^{-8} wt %) yeast; the use of the studied biostimulants in the production of alcohol and biofuel will increase the processes efficiency and the yield of the target products per unit mass of the consumed sugar [77–79];

—potential biostimulants of growth of hydrocarbon-oxidizing bacteria *Rhodococcus erythropolis* in the micro concentration of 10^{-4} – 10^{-8} wt %; this effect can be used in the development of environmentally friendly and cost-efficient approaches to the recovery of environmental objects polluted with oil [80];

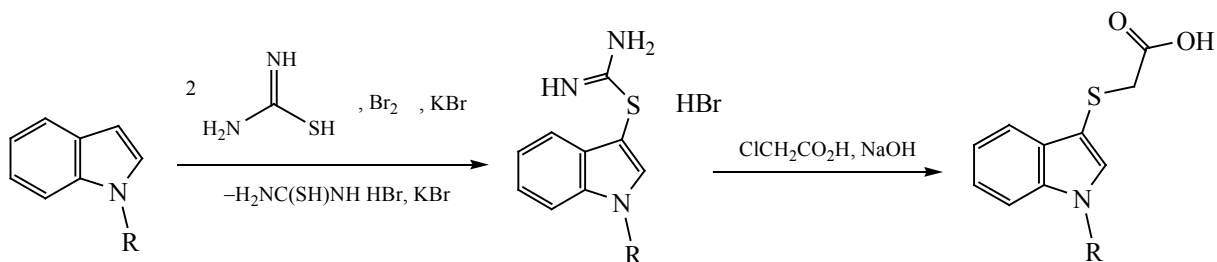
—synthetic biostimulants of malting; the use of micro amount of sulfacetamin (6×10^{-6} g per 1 kg of barley) is the optimal approach reducing the production time, increasing the productivity, and improving the malt quality [81];

—adaptogens and biostimulants of growth of hybrid whitefish; positive action of the protatranes on the increase in size and mass of the fish as well as decrease in its mortality has been revealed [82];

—*N*-methylbis(2-hydroxyethyl)ammonium 2-methylphenoxyacetate (biczazan) has revealed prominent antitumor and antimetastatic activity and absence of toxicity in the *in vitro* systems and in the experiment on animals [83].

Novel efficient method for the synthesis of poorly available 1-R-indol-3-ylsulfanyl(sulfonyl)acetic acids (Scheme 2) for their further conversion into the biologically active hydroxyalkylammonium salts has been suggested in [84, 85]. The approach suggested by the authors has allowed the increase in yield and purity of the products avoiding the formation of side oxidation products (indole disulfides and others), as

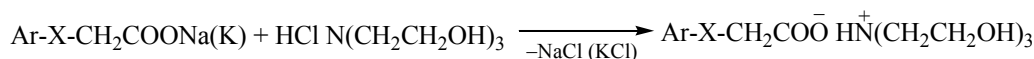
Scheme 2.



Scheme 3.

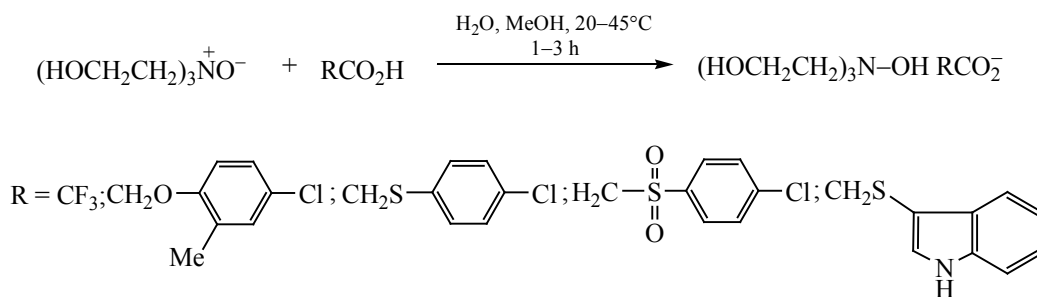


Scheme 4.



Ar = Ph, 2-ClC₆H₄, 4-ClC₆H₄, 2-HOC₆H₄, 2-NO₂C₆H₄, 2-MeC₆H₄, indol-3-yl, 1-benzylindol-3-yl; X = O, S, SO₂, Se.

Scheme 5.



in the case of a strong oxidizer I₂ vapor and KI. The protatranes of 1-R-indol-3-ylsulfanyl(sulfonyl)acetic acids have revealed dose-dependent antiproliferative activity and inhibited spontaneous and mitogen-induced (concanavalin, Con A, Sigma) proliferation of spleen cells in experimental mice.

The interaction of sodium 4-chlorophenylsulfinate with methyl chloroacetate, followed by the hydrolysis of the obtained ester (Scheme 3) is an environmentally friendly and practically feasible method for the synthesis of 4-chlorophenylsulfonylacetic acid (precursor of sulfacetamin). Sulfacetamin has revealed the antithrombotic, membrane-stabilizing, and antioxidant

activity and reduced the level of cholesterol in blood *in vitro* as well as *in vivo*. When applied in low dose, sulfacetamin has revealed prominent immunostimulating and protective-adaptive activity [86].

S.N. Adamovich et al. have elaborated [87] an efficient approach to the synthesis of crezacin and its analogs of pharmaceutical purity (Scheme 4). The authors have noticed that the interaction of TEA with the corresponding aryloxy- or arylsulfanylacetic acids affords the protatranes in high yield (75–90%), but their purity is not sufficient for the application in medicine. The novelty of the suggested method has been the use of TEA hydrochloride (solid, stable, and readily purified

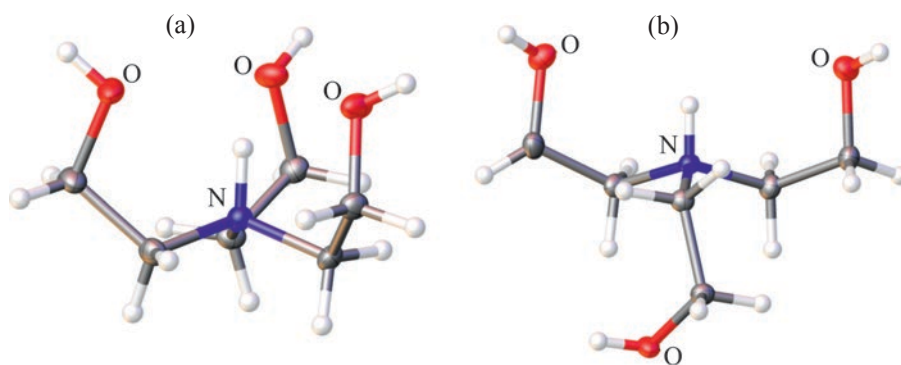


Fig. 4. Conformation of tris(2-hydroxyethyl)ammonium cation: (a) classical tricyclic *endo*-conformation; (b) bicyclic *endo/exo*-conformation [in tris(2-hydroxyethyl)ammonium succinate] [90].

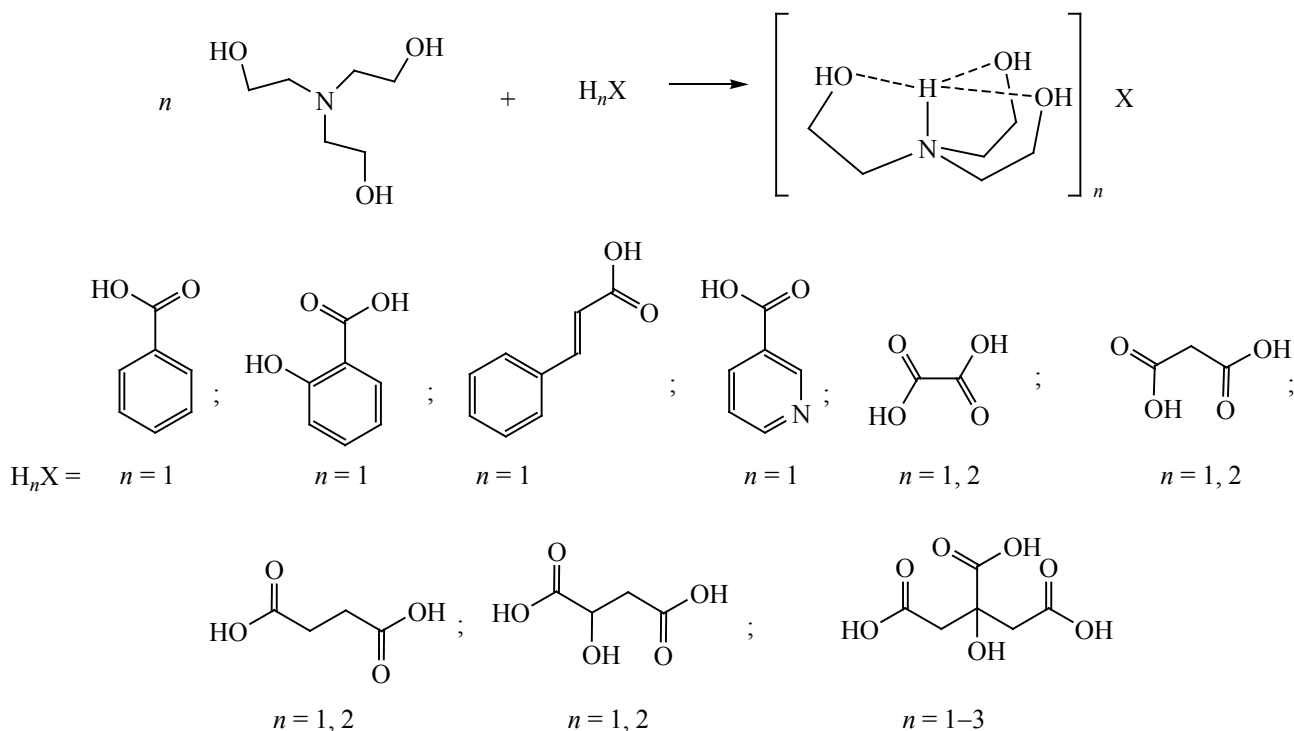
by recrystallization) instead of viscous, hygroscopic, and hardly purified TEA; sodium or potassium salts have been used instead of the free acids.

The reaction of oxatrane with biologically active derivatives of acetic acid has afforded novel analogs of protatranes: tris(2-hydroxyethyl)hydroxylammonium salts (Scheme 5) [88].

Since 2014, the research at the Institute of Silicate Chemistry, RAS has been focused on the synthesis and

investigation of crystal structure of novel protatranes and their analogs. For example, the preparation of tris(2-hydroxyethyl)ammonium salts of benzoic, cinnamic, salicylic, nicotinic, succinic, malonic, oxalic, malic, and citric acids (Scheme 6) has been reported in [89]. Structural studies of these salts have shown that the conformation of the tris(2-hydroxyethyl)-ammonium cation can differ from the usual tricyclic *endo*-conformation [90]. Tris(2-hydroxyethyl)ammonium

Scheme 6.



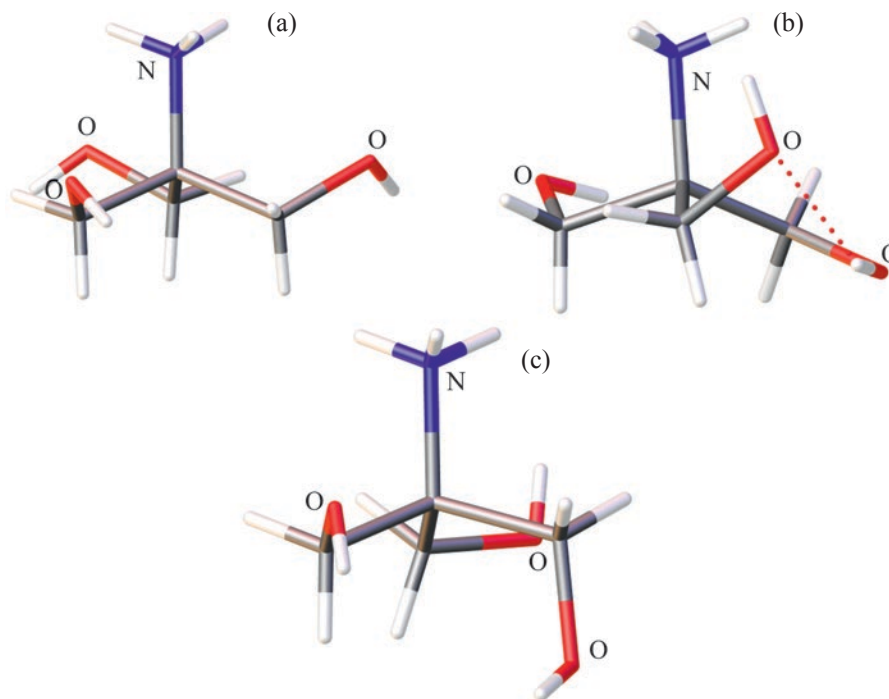


Fig. 5. Three possible conformations of tris(hydroxymethyl)methylammonium cation: (a) planar conformation; (b) *endo/exo*-conformation; (c) *exo*-conformation [93].

succinate is the first tris(2-hydroxyethyl)ammonium salt with bicyclic *endo/exo*-conformation of the cations (Fig. 4b), which form infinite cationic chains via the hydrogen bonds between the N^+H group of a cation and the OH group of the *exo*-branch of the neighbor cation. Surprisingly, the TEA cation conformation in the closest structural analogs, tris(2-hydroxyethyl)ammonium malate and hydrosuccinate, corresponded to the tricyclic *endo*-conformation (Fig. 4a) [90, 91].

In [91, 92] it has been shown that tris(2-hydroxyethyl)-ammonium salts of carboxylic acids are protic ionic liquids (mp < 100°C) exhibiting growth-stimulating and antimicrobial action. The investigated ionic liquids have revealed selective activity towards *Staphylococcus aureus* bacteria. Tris(2-hydroxyethyl)ammonium salts of cinnamic, benzoic, and malonic acids have exhibited positive action on the germination and growth of watercress (*Lepidium sativum* L.). Their use as growth stimulants for the *Rhizopus oryzae* fungi, promising chitosan producer, has allowed significant increase in the yield of the obtained biosorbent (to 24%).

Further research at Institute of Silicate Chemistry, RAS have been focused on the synthesis of novel hydroxyalkylammonium salts. For example, tris(hydroxymethyl)methylammonium (TRIS) and tris(2-hydroxypropyl)ammonium (TPA) salts of analogous carboxylic acids (cinnamic, benzoic, etc.) have been obtained for the first time [93, 94] to investigate the conformation of the hydroxyalkylammonium cation and the cation-anion interactions. In the case of tris(hydroxymethyl)-methylammonium cation, three conformations have been revealed (Fig. 5): (a) planar, in which three hydroxymethyl groups are in the plane with the quaternary carbon atom (Fig. 5a); (b) rare *endo/exo*-conformation, in which one of the branches is shifted towards the N^+H_3 group (*endo*-branch), the second one is planar, and the third is slightly off the carbon atom plane towards the opposite direction (*exo*-branch) (Fig. 5b); (c) *exo*-conformation, in which two branches are in the plane, and the third branch is significantly deviating oppositely to the N^+H_3 group (Fig. 5c). Analysis of the crystallographic database has shown that the planar conformation is more typical of the TRIS salts.

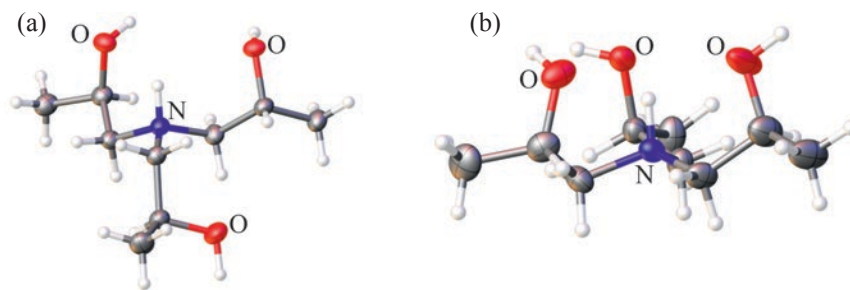


Fig. 6. Conformation of TPA cation: (a) bicyclic *endo/exo*-conformation, (b) tricyclic *endo*-conformation [94].

In the case of the TPA salts, the probability of formation of the bicyclic *endo/exo*-conformation is significantly higher than for the TEA salts, likely due to the presence of three additional methyl groups in the TPA cations. However, the formation of the tricyclic *endo*-conformation of the TPA cations is also possible (Fig. 6). Surprisingly, two polymorph modifications with different conformations of the TPA cations (tricyclic and bicyclic) have been found for tris(2-hydroxypropyl)ammonium salicylate [94].

Joint research with Granov Russian Scientific Center of Radiology and Surgical Technologies [95, 96] have shown that the synthesized hydroxyalkylammonium carboxylates are promising buffering agents for the preparation of gallium-68 complexes with chelators and peptides. The ^{68}Ga complexes with a series of clinically important peptides are radiopharmaceuticals important in the nuclear medicine for the diagnostics of various neoplasms. Hydroxyalkylammonium buffers based on TEA benzoate and 2-methylphenoxyacetate have been the most efficient in ^{68}Ga -labeling reactions of peptides at low temperature (37°C). Their efficiency has significantly exceeded that of commercially available and widely used HEPES buffer.

Another novel direction is the use of biologically active protatranes as environmentally friendly biocides in protective coatings. Biostability of the organosilicate coatings containing 1 or 3 wt % of protatrane of salicylic acid as a mild biocide has been studied in [97]. The organosilicate coatings based on polydimethylphenylsiloxane containing the biocide as well as without it have revealed high biostability.

However, the coating containing 3 wt % of the biocide additive has shown the best biostability.

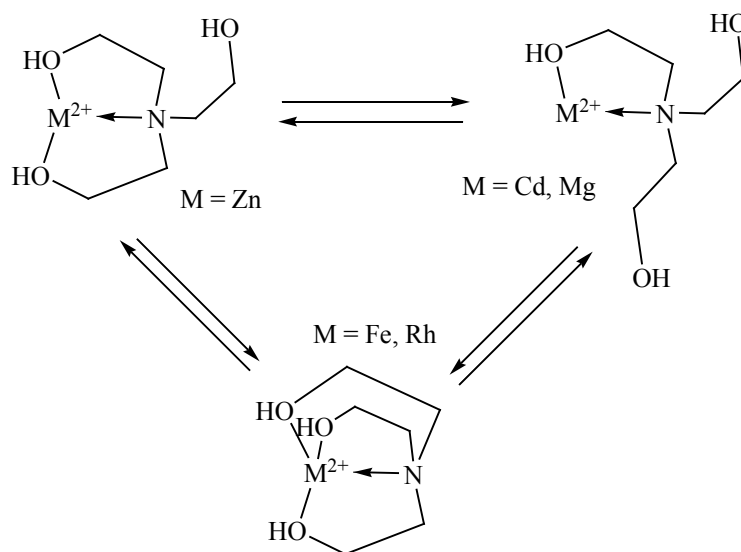
5. HYDROMETALLATRANES

The studies of hydrometallatranes in the group of M.G. Voronkov were started much later in comparison with the research on the protatranes. The preparation of novel representatives of hydrometallatranes was reported only in early 2000s. For example, M.G. Voronkov et al. [98, 99] have synthesized a series of biologically active TEA complexes with salts of the aroxyacetic acids. Crystal structure of one of them, $[\text{Ni}(\text{TEA})_2][4\text{-ClPhSCH}_2\text{CO}_2^-]_2$, has been elucidated by means of X-ray diffraction analysis [100]. The synthesized complexes consisting of the hydrometallatrane cations and protic acid anions have been assigned to the class of metalated alkanolammonium ionic liquids by the authors of [100–103].

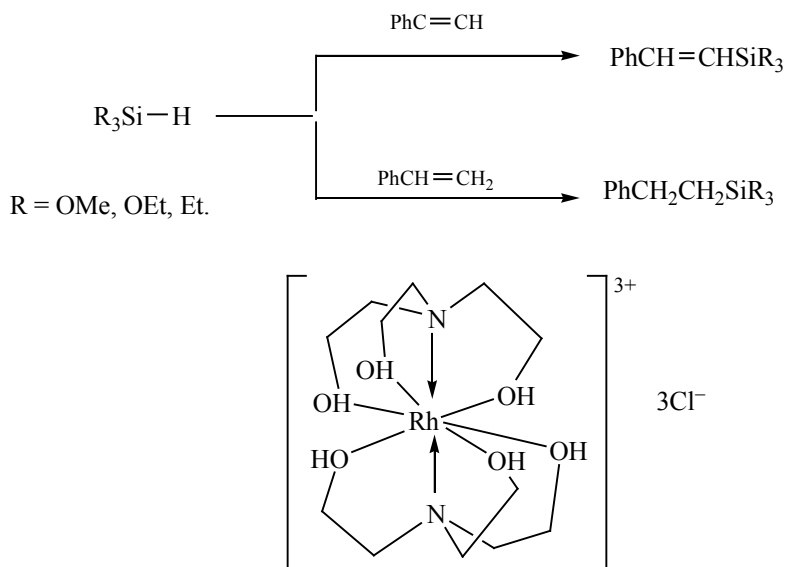
The study of the hydrometallatranes by means of NMR spectroscopy [101–103] has shown that the equilibrium between the mono-, bi-, and tricyclic complex structures is established under the biomimetic conditions (water, 25°C). The equilibrium shift is dependent on the metal nature (Scheme 7) as reflected in the NMR spectral parameters.

Investigation of the biological activity of the hydrometallatranes initiated by M.G. Voronkov has resulted in the discovery of new antidotes of heavy poisoning with ethanol and carbon monoxide. The developed antidotes are the TEA complexes with zinc salts of inorganic and organic acids (2,8,9-trihydrozincatrane) [104, 105]. Low-toxic (LD_{50} 675–4000 mg/kg) efficient compounds exhibiting immunoactive properties

Scheme 7.



Scheme 8.

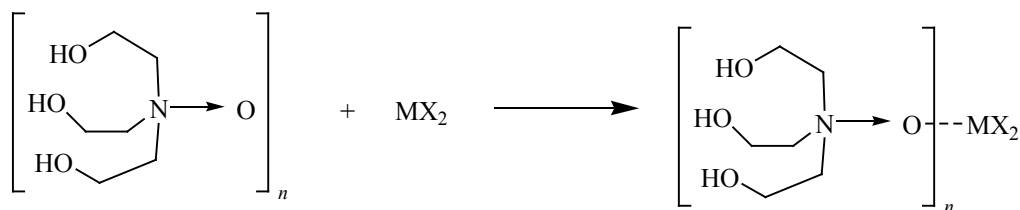


(immunostimulating or immunosuppressive action) have been recognized among the TEA complexes with the salts of biotrace elements (Mg, Ca, Zn, Mn, Cu, Fe, Co, Ni, Cd, and Rh) *in vitro* and *in vivo* [106, 107]. Depending on the concentration and the nature of metal, Zn(II)-, Cu(II)-, Mn(II)-, and Ni(II)-containing TEA complexes can promote or suppress the growth activity of suspension culture of the sugar-cane cells (*Saccharum officinarum*, sort POJ2878) [18].

The TEA complex with zinc methylphenoxyacetate also known as zincatrane or citrimin deserves special attention among the hydrometallatranes. Intensive investigation of its biological activity has revealed:

- the efficiency of zincatrane in the treatment and prevention of atherosclerosis significantly exceeding that of trecresan (the required dose being 5 times lower) [109];

Scheme 9.



– inhibition of the synthesis of acid cholinesterase of thrombocytes and mononuclear leucocytes by zincatran [110, 111];

—inhibition of acid phospholipase A1 and suppression of general activity of alkaline phospholipase A2 of mononuclear leucocytes by zincatran [114, 115]

—promotion of the expression of matrix RNA of tryptophanyl-tRNA-synthase (exhibiting prominent antiangiogenic and antiatherogenic action) by zincatran [112–116];

—the efficiency of zincatran in the treatment of thermal burn wounds of skin, especially in combination with phototherapy [117];

—the application of zincatran as biologically active additive for the enhancement of static and dynamic ability to work [118];

—zincatran-stimulated expression of the gene of coactivator PGC-1 α , the use of which increases the content of mitochondria in the muscle tissue and enhancement in the ability to work of the cross-stripped muscular system [119].

Adamovich et al. [120] have been the first to demonstrate the ability of the $[\text{Rh}(\text{TEA})_n]\text{Cl}_3$ ($n = 1, 2$) hydrometallatranes to catalyze regioselective hydrosilylation of phenylacetylene and styrene (Scheme 8).

The synthesis of novel hydrometallatranes derivatives $[(\text{HOCH}_2\text{CH}_2)_3\text{NO}]\cdot\text{MX}_2$ based on the oxatrane complexes with transition metal salts (Scheme 9) has been reported for the first time in [121].

At the Institute of Silicate Chemistry, RAS, the research has been more focused on the preparation and structure investigation of the hydrometallatranes based on the hydroxyalkylamines complexes with essential biometals carboxylates $\text{M}(\text{RCO}_2)_n$ [$\text{R} = \text{C}_6\text{H}_5, 2\text{-OHC}_6\text{H}_4, \text{C}_6\text{H}_5\text{CHCH}, \text{CH}_2\text{CH}_2\text{CO}_2$, etc., $\text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II}),$

$\text{Zn}(\text{II}), \text{Ni}(\text{II}),$ etc., $n = 1, 2$] or their inorganic salts MX_n ($\text{X} = \text{Cl}, \text{NO}_3, \text{SO}_4$, etc., $n = 1, 2, \text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II}), \text{Zn}(\text{II}), \text{Ni}(\text{II}),$ etc.). A broad range of new hydrometallatranes and their closest analogs with TEA, TRIS, DEA, and TPA ligands have been synthesized during recent 5 years.

Intensive study of the hydrometallatranes structure has revealed that it is strongly affected by the nature of the metal and the solvent, the presence of additional ligands and their denticity. For example, mononuclear cationic complexes consisting of the $[\text{M}(\text{TEA})_2]^{2+}$ [$\text{M} = \text{Cu}(\text{II}), \text{Co}(\text{II})$] cations and anions of inorganic (NO_3^-) or carboxylic acids ($[\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2]^{2-}, \text{C}_6\text{H}_5\text{CHCHCO}_2^-$), mononuclear mixed-ligand complex $[\text{Zn}(\text{TEA})(\text{H}_2\text{O})_2]\text{SO}_4\cdot\text{H}_2\text{O}$, and binuclear mixed-ligand complexes: $[\text{Zn}_2(\text{TEAH}_2)(\text{C}_6\text{H}_5\text{CO}_2)_3]$, $[\text{Cu}_2(\text{TEAH}_2)_2(2\text{-OHC}_6\text{H}_4\text{CO}_2)_2]\text{H}_2\text{O}$, $[\text{Cu}_2(\text{TEAH}_2)_2(\text{C}_6\text{H}_5\text{CHCHCO}_2)_2]\text{H}_2\text{O}$, $[\text{Co}_2(\text{TEA})_2(\text{NO}_3)_2(\text{C}_4\text{H}_4\text{O}_4)]$, and $[\text{Co}_2(\text{TEA})_2\text{Cl}_2]\text{Cl}_2$ have been prepared in [122–124].

An original approach to the synthesis of the hydrometallatranes, based on the interaction of two cationic TEA complexes, has been suggested in [122]. A binuclear mixed-ligand $\text{Co}(\text{II})$ complex has been prepared using this approach (Scheme 10).

The trimethylhydrometallatranes, complexes of tris(2-hydroxypropyl)amine (TPA) with $\text{Ni}(\text{II}), \text{Zn}(\text{II}), \text{Cu}(\text{II}),$ and $\text{Co}(\text{II})$ salts of bioactive carboxylic acids have been synthesized for the first time. It has been shown by means of single-crystal X-ray diffraction analysis that the structure of TPA complex with nickel(II) cinnamate corresponds to the cationic mononuclear complex consisting of the cinnamate anions and the $[\text{Ni}(\text{TPA})_2]^{2+}$ cations with tridentate TPA coordination, as in the case of the mononuclear cationic TEA complexes (Fig. 7) [125].

The complexes of copper(II), zinc(II), nickel(II), and cobalt(II) L-valinates with TEA, DEA, and TRIS, the formation of which has been confirmed by a set of

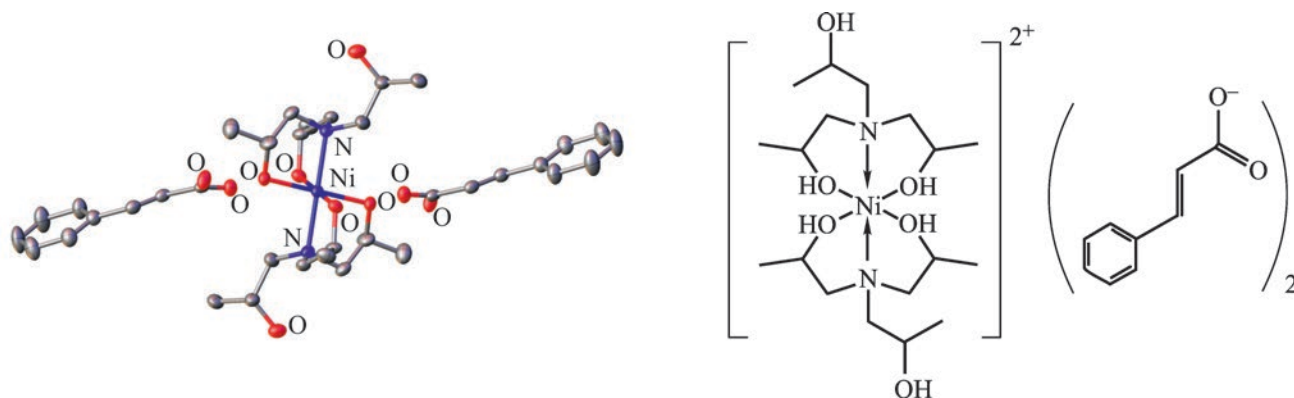


Fig. 7. Molecular structure of the $[\text{Ni}(\text{TPA})_2](\text{C}_9\text{H}_7\text{O}_2)_2$ complex [128].

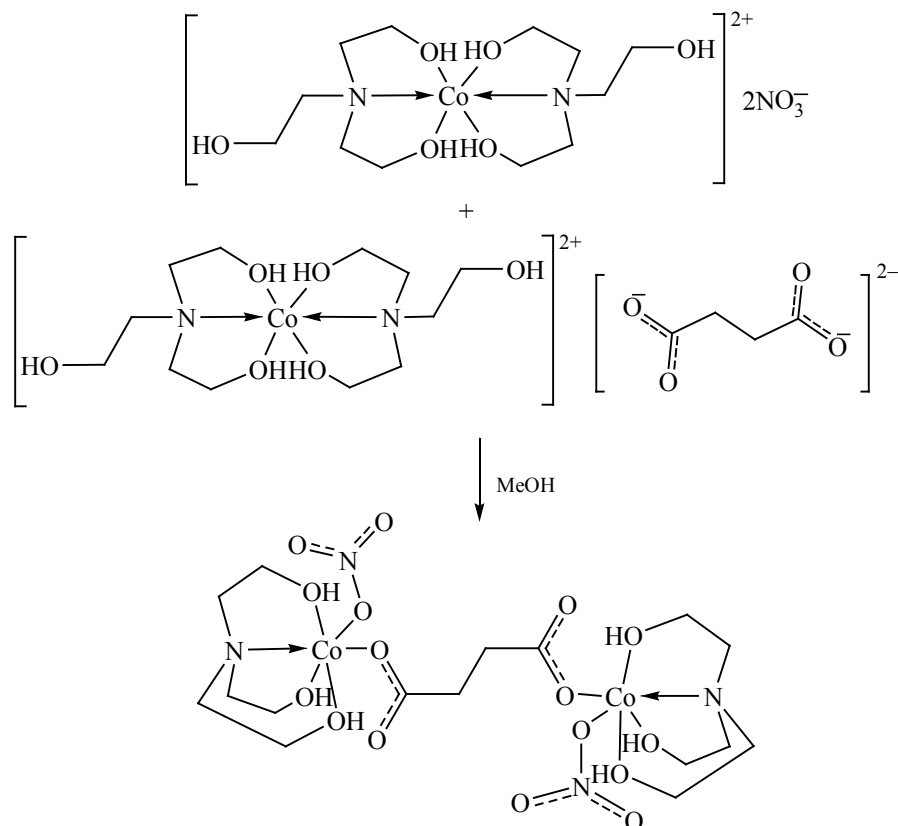
methods, have been obtained for the first time in [126]. The complex of cobalt valinate with TRIS has revealed the broadest activity towards the *S. aureus*, *A. niger*, and *M. tuberculosis* microorganisms.

In [127] it has been shown that the cationic complex of Co(II) cinnamate with TEA ($[\text{Co}(\text{TEA})_2](\text{C}_9\text{H}_7\text{O}_2)_2$) exhibits high activity with respect to the micromycetes (*Aspergillus niger*, *Cladosporium cladosporioides*,

and *Penicillium brevicompactum*), major materials destructors, and can be recommended as a promising environmentally friendly biocide additive to the protective materials and coatings.

The use of hydrometallatranes as environmentally friendly biocide components of protective antifouling coatings has been demonstrated for the first time in [128]. The composition containing a mixture of protatranes

Scheme 10.



of salicylic acid and the $[\text{Zn}_2(\text{TEAH}_2)(\text{C}_6\text{H}_5\text{CO}_2)_3]$ hydrometallatrane as the biocide additive has been found the most promising among the considered paint-and-lacquer coatings for further development.

6. CONCLUSIONS

In summary, the studies of atranes initiated by M.G. Voronkov in the second half of the last century have remained important. Academician Mikhail G. Voronkov has developed a unique interdisciplinary direction of modern science, the results of which are widely used in medicine, pharmaceuticals, agriculture, microbiology, and other fields. The development of trescan drug has led to the discovery of new biologically active protatranes, potential drugs. The protatranes have been recently recognized as protic ionic liquids which are of special interest to science and technology. Recent research on the protatranes has led to novel aspects of their application, as buffering agents in the radiolabeling reactions of biomolecules and as new-generation biocide components of protective composites.

The number of reports on the synthesis of hydro-metallatranes with different hydroxyalkylamines has kept growing. The study of their biological activity initiated by M.G. Voronkov are unique. The research on metal-organic frameworks (coordination polymers consisting of metal ions or small clusters linked to organic ligands with the formation of mono-, two-, and three-dimensional structures) are currently under development. The polymeric complexes of hydroxyalkylamines with metal carboxylates are the metal-organic frameworks. Owing to the porous structure of the metal-organic frameworks, their application range is broad, from gas adsorption and catalysis to targeted drug delivery and biosensors. These facts evidence the urgency and practical importance of the research in the field of the atranes, the development of which has been invaluablely contributed by an outstanding scientist, Academician Mikhail G. Voronkov.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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