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ANNIVERSARIES AND DATES

A. N. NESMEYANOV INSTITUTE OF ORGANOELEMENT COMPOUNDS (INEOS), RUSSIAN ACADEMY OF SCIENCES: 50 YEARS

This year the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS), one of the leading chemical institutes of the Russian Academy of Sciences, observes its 50th anniversary. The Institute was created in 1954 within the N. D. Zelinsky Institute of Organic Chemistry.

A tremendous contribution to the creation and growth of INEOS was made by the outstanding scientist who directed the Institute for 26 years and was President of the Academy of Sciences of the USSR (1951-1961): Academician A. N. Nesmeyanov, creating the new heteroorganic chemistry as an independent scientific discipline linking organic chemistry, coordination chemistry, and inorganic chemistry. In 1980, the Institute was named after A. N. Nesmeyanov. The next directors of the Institute were Academicians A. V. Fokin (1980-1988) and M. E. Vol'pin (1989-1996). Since 1996, the director of the Institute has been Academician Yu. N. Bubnov.

The international reputation of the Institute is associated with the names of the outstanding scientists who initiated new research directions in organic, heteroorganic, polymer, and physical chemistry and physics such as Academicians K. A. Andrianov, M. E. Vol'pin, M. I. Kabachnik, I. L. Knunyants, V. V. Korshak, I. V. Obreimov, S. R. Rafikov, O. A. Reutov, and A. V. Fokin; Corresponding Members of the Academy of Sciences D. N. Kursanov, Yu. T. Struchkov, and R. Kh. Freidlina. The well-known professors V. T. Aleksanyan, N. F. Anisimov, V. M. Belikov, D. A. Bochvar, N. N. Bubnov, N. I. Gel'man, L. S. German, A. A. Zhdanov, L. I. Zakharkin, A. I. Kitaigorodskii, A. F. Kolomiets, A. M. Sladkov, V. A. Sergeev, V. N. Setkina, M. I. Rybinskaya, D. Ya. Tsvankin and others have worked at INEOS.

INEOS is one of the leading scientific centers in the field of heteroorganic and polymer chemistry. The following major scientific research directions have been established and successfully developed at the Institute:

– development of new methods for synthesis of heteroorganic compounds and their application in organic synthesis and catalysis;

– basic research in the field of heteroorganic and organic chemistry, including study of new structures, chemical reactivity and kinetics;

– creation of new methods for catalytic asymmetric synthesis;

– obtaining biologically active compounds with a broad spectrum of action for use in medicine and agriculture;

– study of fundamental problems in the synthesis, structure, and properties of polymers and composites, various heteroorganic and organometallic polymers, and methods for introducing organometallic and metallic fragments into a polymer matrix;

– study of new experimental approaches to analysis of organic and heteroorganic compounds.

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New structures and classes of heteroorganic compounds have been predicted and synthesized and a number of internationally recognized discoveries have been made at INEOS. Carboranes (boron framework compounds) and then many carborane derivatives were obtained here (L. I. Zakharkin, 1963). A third form of carbon was discovered and studied: carbyne (V. V. Korshak, A. M. Sladkov et al., 1971), with cumulated and conjugated bonds. A fourth form of carbon, fullerene C60, was predicted by theorists at the Institute (D. A. Bochvar and E. G. Gal'pern, 1973) and brilliantly confirmed in subsequent experiments by foreign scientists in 1985. Work on chemical binding of molecular nitrogen (M. E. Vol'pin and V. B. Shur, 1967) and other small molecules under mild conditions has been internationally recognized. In 1973, the phenomenon of 1,2-rearrangement of polyhalogenated aliphatic radicals in the liquid phase was observed (A. N. Nesmeyanov, R. Kh. Freidlina et al.). In 1966, electrophilic ionic hydrogenation was discovered, which makes it possible to reduce alkenes, carbonyl compounds, and heteroaromatic compounds, including thiophenes (D. N. Kursanov and Z. N. Parnes et al.). In 1992, a certificate was awarded for the discovery of the "Ability of achiral molecular structures to help recognize enantiomers," (V. A. Davankov, S. V. Rogozhin et al.), which led to ligand-exchange chromatography. Finally, in 1998 the discovery of "The phenomenon of cyclic migration of an unpaired electron through polyvalent atoms of non-transition elements" was recorded (M. I. Kabachnik et al.).

Closely associated with the name of the Institute is the concept of "synthetic food," including "synthetic caviar," where development of the latter was used as an example by a group of Institute staff members, under the direction of S. V. Rogozhin and G. L. Slonimskii, of implementation of the idea of A. N. Nesmeyanov concerning application of advanced chemical technology methods to include inefficiently utilized natural proteins in human nutrition. Many processes have been developed and many materials have been created for both technical and biomedical purposes using inventions of the Institute: Ferroceron, VIK and PORK, Perfluoran, Ftorazol, Fluoroxane, Aman, Loeran, Cyacrin, Carbyne, Vitlan, Bloksil, Vinalan, Etilan, Styrosorb, and also the recently created Carbylan, Porocoll, Bupranal, and Intercide.

INEOS today is a large research center where 760 people work, including 558 scientists (2 Academicians, 4 Corresponding Members, 78 Doctors and 262 Candidates in the sciences). Organizationally, the Institute includes 58 science laboratories and research groups. About 2000 scientific papers and 13 monographs have been published on the results of scientific research conducted over the past five years. In those years, mutually advantageous contracts have been concluded with more than 150 universities, institutes, and industrial centers in Russia and abroad. In the past 20 years, the Institute has participated in the organization of more than 100 conferences, symposia, and seminars.

INEOS was awarded the Order of Lenin for major achievements in 1967. Institute staff have been awarded 8 Lenin Prizes, 30 State Prizes, and the Russian Federation Government Prize in the field of science and technology; 4 Institute staff members have been honored with the title Hero of Socialist Labor, 9 individuals have been named Honored Scientist of the Russian Federation, and one has been named Honored Inventor of the RSFSR.

One of the most important forward-looking tasks of the Institute is training of highly educated young specialists with extensive knowledge and mastery of the entire arsenal of modern research methods, which is possible only by integrating the educational process and basic scientific research while drawing on the scientific potential and technical instrumentation of the institutes of the Russian Academy of Sciences. In order to meet this challenge in the fields of heteroorganic chemistry, the physical chemistry of polymers, the chemistry of biologically active compounds, and biomedical chemistry, 6 scientific teaching centers were created within INEOS which today have been transformed to the Science Education Center (Russian Academy of Sciences), INEOS Division. The Center includes a division for training INEOS scientists (graduate program) and the basic departments: *Organometallic Chemistry*, jointly with the Chemistry Department of M. V. Lomonosov Moscow State University; *Biomedical Chemistry* and *Organosilicon and Inorganic Polymers,* jointly with the D. I. Mendeleev Russian Chemical Technological University; *Physiologically Active Compounds,* jointly with the M. V. Lomonosov Moscow State Academy of Fine Chemical Technology; *Physical Chemistry of*

Polymers, jointly with the Physics Department of Moscow State University; and *Physical Research Methods in Chemistry,* jointly with the Higher Chemical College of the Russian Academy of Sciences. More than 2000 students total have obtained specialized higher education at the INEOS Science Education Center of the Russian Academy of Sciences. More than 80 INEOS scientists participate in teaching lecture courses and conducting seminar and laboratory work with the students.

From the very beginning of INEOS, there has been an organic linkage between synthetic and theoretical research in the field of heteroorganic and polymer chemistry on the one hand and all the required physical and physicochemical research on the other hand, so the scientific activity of many INEOS laboratories is at the junction between several branches of chemistry and physics. As A. N. Nesmeyanov said metaphorically, this defines the "growth points" of modern scientific and technical progress. In addition to traditional time-tested interdisciplinary sciences (including the chemistry of heteroorganic compounds itself), the accumulated valuable experience has given birth to a number of new scientific research directions characterized by a unique linkage of knowledge in the fields of organic chemistry, heteroorganic chemistry, coordination chemistry, physical chemistry, and the chemistry of high molecular weight compounds and natural biologically active compounds.

Thus a new research direction appeared at the junction of organic, organometallic, and coordination chemistry: the chemistry of organic compounds of transition metals, π-complexes of metals and clusters. The unique properties of these compounds made it possible to create new organometallic catalysts and to develop processes for activation of small molecules, including nitrogen, carbon oxides, hydrocarbons, etc. Linkage of organic and heteroorganic chemistry on the one hand and modern experimental and theoretical methods of physical chemistry on the other hand led to growth of research on reactivity and obtaining fundamentally new data in the area of the structural chemistry and molecular dynamics of heteroorganic compounds.

Linking heteroorganic chemistry, biochemistry, pharmacology, and toxicology made it possible to discover the secrets of the mechanisms responsible for the effect of organophosphorus compounds on biological structures and living organisms. Significant progress was achieved in the area of new anticancer drugs with selective action and physiologically active heteroorganic compounds, including fluorine-containing compounds. A number of functional derivatives of the *closo*-dodecaborate anion have been synthesized; optically active aminocarboranes and aminocarborane-based derivatives have been obtained, which are of great interest for use in boron neutron capture therapy for cancer; and stereoselective synthesis of ferrocenyl alkyl azoles, which have an antitumor effect, has been accomplished.

Considerable advances have been made in the area of heterocyclic compounds. An original method has been discovered for obtaining bicyclic and tricyclic heterocycles with a bridging nitrogen atom, containing an aziridine moiety, based on reductive allylation of 3,5-dibromopyridine and 4-bromoisoquinoline, metathesis reactions with ring closure catalyzed by ruthenium carbenium complexes; and a series of derivatives of cyclic α-polyfluoromethyl α-imino acids have been obtained with five-membered, six-membered, and seven-membered rings. Based on derivatives of pyridine, proline, and chiral amines, new catalysts have been created with chiral centers in amine moieties and/or with a chiral phosphorus atom, and new substrates for a large number of asymmetric reactions: phase-transfer alkylation of CH-acids, allyl sulfonylation, amination, and alkylation, making it possible to achieve record-breaking chemical and enantiomeric yields. Unique optically active palladium complexes of C_{60} and C_{70} fullerenes have been synthesized with two axially chiral diphosphine ligands in the dithienyl series, which are efficient catalysts for homogeneous enantioselective hydrogenation. Original methods have been developed for constructing azabicyclodecadienes and azaspiroalkenes, based on two sequential processes: reductive allylboration of pyridines, isoquinolines, and lactams, leading to diallylated nitrogen-containing heterocycles, and intramolecular metathesis catalyzed by a Grubbs ruthenium catalyst. The bicyclic and tricyclic systems obtained are the basic structural components for a number of important alkaloids (cytisine etc.) For a number of novel pyridazino[4,3-*b*]indoles, a connection has been discovered between the high antitubercular activity, the monooxidase inhibiting effect, and the *ortho* effect of the 4-aryl substituent.

Work at the junction of organic and inorganic chemistry, study of polymer formation processes and also structure–property relations led to development of the chemistry of polymers with heteroorganic and inorganic chains of molecules, and has opened up routes to new classes of linear, bilinear, and network polymers and dendrimers. Based on these polymers, materials have been developed with high thermal, catalytic, sorption, and electrophysical characteristics, structural plastics, heat-stable composites and adhesives, membranes and polymers for electronics and medicine. Research in the area of heteroorganic and organic chemistry includes the study of new structures, chemical activity and kinetics, the study of organometallic and coordination complexes with σ-, π-, and *n*-bonds, the development of new methods for synthesis of heteroorganic compounds with polyhedral substituents (carboranes, fullerenes), multidecker compounds, clusters, anti-crowns, and also the study of their geometry, electronic structure, and chemical behavior (stereochemistry, tautomerism, molecular dynamics) by modern experimental and calculation methods. An important role is played by use of organometallic compounds in asymmetric synthesis and catalysis. A number of laboratories have been successfully working on obtaining biologically active compounds with a broad spectrum of action for use in medicine and agriculture.

Broad studies have been conducted on fundamental problems in the synthesis, structure, and properties of polymers and composites, and computer-assisted design of macromolecules has improved methods for synthesis of monomers and polymers. An important role is played by synthesis of aromatic and heterocyclic polymers, including polyconjugated, ultrarigid, and network polymers, the study of their physical and physicochemical properties, and study of heteroorganic and organometallic polymers and methods for introducing organometallic and metallic fragments into a polymer matrix. Nanostructures in polymers and synthesis of different types of nanoparticles using polymer systems as well as liquid-crystal polymers and their properties have been widely studied; studies have been conducted on the properties of polyelectrolytes; and processes of modification of polymers have been investigated, including surface modification, thermal and photochemical conversions in organic and heteroorganic polymers.

Among the interesting results of studies conducted by Institute staff, we may note the synthesis of multidecker sandwich metallocenes, synthesis of novel classes of δ-, π-, and mixed complexes of metals with olefins, acetylene, vinylidene, and cumulene ligands, novel types of clusters, azole complexes, etc. There has been development of the chemistry of cyclopentadienyl carbonyl compounds of transition metals, the most interesting of which is cymantrene, an effective antiknock compound. Aluminum, tin, boron, fluorine, phosphorus, etc. derivatives are widely used in modern organic synthesis, and INEOS has also developed synthesis methods for these compounds. The first examples were obtained of anti-crown complexes, containing three mercury atoms in the macrocycle, with a complicated complexed hexacyanoferrate anion, which expands the limits for practical application of these unusual crown compounds.

Metallocenes have been used as the basis for synthesizing next-generation chelate complexes of rhodium, iridium, and platinum containing tridentate P–C–P ligands, which can be used in production of very important raw material for petrochemistry and an environmentally friendly energy carrier (hydrogen) and in fuel cells.

At the Institute, considerable attention has been focused on medical, environmental, conversion, and other practical problems. Polyacrylic acid and hydroxyapatite have been used as the basis for creating original biocompatible polymer/mineral implants for maxillofacial surgery ("artificial bone"). An environmentally friendly method has been developed for synthesis and modification of polymers in supercritical media. Micellar polymerization in aqueous medium has been used to synthesize self-associating hydrophobically modified ternary copolymers (terpolymers). The studies conducted made possible targeted control of the properties of gels depending on the practical problems to be solved, especially for enhancement of petroleum recovery. Samples have been obtained of carbon-containing suture monofilaments (Vitlan filaments) equipped with atraumatic needles, which are better for biomedical purposes than the threads used in surgical practice. Radiative matrix/gas-phase copolymerization on stretched polyamide films has been used to obtain polymer semiconductors with a fundamentally new structure and high electrical conductivity. The novel materials may be used in various areas, in particular for creating cheap large solar batteries. The activating effect of new reaction media (environmentally friendly ionic liquids obtained on the basis of imidazole) on polymer formation processes has been established.

Methods have been developed for obtaining cheap and efficient bidentate extraction agents and sorbents for transuranium elements: methylcarbamoyl methylphosphinic acids and their derivatives. A series of phosphite, phosphate, and phosphonate fire-extinguishing agents, based on lower primary alkanols and polyfluoroalkanols, have been obtained that are more effective than trifluorobromomethane (the production of which is banned by the Montreal protocol). Catalysts have been discovered for polycyclotrimerization of diisocyanates that simultaneously function as dyes. This makes it possible to synthesize colored gradient polymer materials that are ready for practical use. Development and supply of improved cyanoacrylate composite for electronics technology products continues. A synthesis method based on 2,4,6-trinitrotoluene has been developed for a monomer whose polymerization with dianhydrides of aromatic tetracarboxylic acids yields film-forming polyamides that are soluble in organic solvents and combine high thermal and mechanical characteristics with a low dielectric constant, which means they can be used as interlayer insulators for multiple integrated circuits. In conjunction with the S. A. Lavochkin Design Bureau, polymer coatings have been created for friction assemblies capable of operating exposed in outer space, resulting in prolonged functionality of aerospace systems and apparatus.

More detailed information about the Institute and its staff can be found at the Institute website (http:/www.ineos.ac.ru).

Yu. N. Bubnov and K. A. Kochetkov

The Editorial Board of this journal is pleased to offer our regards to all at INEOS on the day of its happy anniversary. Our anniversary wish for you all is new brilliant ideas and outstanding achievements in both science and practical implementation of your developments.

We hope that our fruitful cooperation continues to grow.