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A N Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences



This issue of the Journal comprises reviews written by researchers of the A N Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences (INEOS), one of the leading chemical research institutes of the Russian Academy of Sciences. This year INEOS is celebrating its 50th anniversary.

The Institute was founded in 1954 on the initiative of Academician A N Nesmeyanov on the basis of several laboratories of the N D Zelinsky Institute of Organic Chemistry concerned with organoelement (organometallic) and polymer chemistry.

Academician A N Nesmeyanov, who was President of the USSR Academy of Sciences in that period (1951 – 1961), became the first director of INEOS and remained in this post until 1980. In later periods, the Institute was directed by Academicians A V Fokin (1980 – 1988) and M E Vol'pin (1989 – 1996). Since 1996, INEOS has been headed by Academician Yu N Bubnov.

From the very beginning, research activities at INEOS were envisaged as a harmonious combination of synthetic and theoretical studies; therefore, investigations in many laboratories of the Institute were carried out at the junction of different branches of chemistry and physics. According to the figurative expression of Academician A N Nesmeyanov, this trend has charted the 'points of growth' in the development of modern science and technology. Following this principle, the chemistry of organic compounds of transition metals, π-complexes of metals and clusters has emerged at the interface between organic, organometallic and coordination chemistry. The unique properties of these compounds have enabled the preparation of novel organometallic catalysts and the development of processes for activating small molecules, such as nitrogen, carbon oxides, hydrocarbons, *etc*. A combination of organic and organoelement chemistry with modern experimental and theoretical methods in physical chemistry has fostered investigations into reactivities of organic and organoelement compounds which in turn has made it possible to obtain new in principle data on their structures and molecular dynamics.

At present, INEOS is one of the leading research centres in the area of organoelement and polymer chemistry. The main investigations carried out by the Institute are developing successfully along the following lines:

— development of novel methods for the synthesis of organoelement compounds and their application in organic synthesis and catalysis;

— fundamental studies in the field of organoelement and organic chemistry including investigations of novel structures, chemical activities and kinetics;

— development of novel methods of catalytic asymmetric synthesis;

— synthesis of biologically active compounds possessing a broad range of action for their possible use in medicine and agriculture;

— fundamental studies of the synthesis, structure and properties of polymers and composites, organoelement and organometallic polymers; development of methods for introducing organometallic and metallic fragments into polymeric matrices;

— development of novel experimental approaches to the analysis of organic and organoelement compounds.

Other remarkable achievements of the Institute researchers in the field of development of novel methods for the synthesis of organoelement compounds and their application in organic synthesis and catalysis over the past decade include synthesis of

multidecker sandwich-type metallocenes, of novel classes of σ-, π- and mixed metal complexes with alkene, acetylene and vinylidene ligands, of organoelement compounds with polyhedral substituents (carboranes and fullerenes) and of novel Hg-containing anticrowns binding complex anions, which significantly expands the range of practical applications of these unusual compounds. A new generation of rhodium, iridium and platinum chelate complexes based on metallocenes conjugated to tridentate P,C,P ligands synthesised in INEOS can find use in hydrogen production. Methods have been developed for the synthesis of methylcarbamoylmethylphosphinic acids and their derivatives as inexpensive and efficient bidentate extractants and sorbents of transuranium elements, from raw materials in the framework of a conversion programme. Flame suppressants based on phosphites, phosphates and phosphonates of lower primary alkanols and polyfluoroalkanols, which surpass currently used trifluorobromomethane banned by the Montreal Protocol in efficiency, have also been prepared.

The most impressive results in the field of chemistry of polymers and composites include synthesis of a novel class of polymers consisting of organoelement and inorganic chains, of polymers with remarkable thermal, catalytic, sorption and electrophysical properties; preparation of engineering plastics, thermostable composite materials and adhesives, membranes and polymers for electronic engineering and medicine; synthesis of novel aromatic and heterocyclic polymers including polyconjugated, super-rigid and network polymers. Special attention is given to the development of procedures for introducing organometallic and metallic fragments into a polymeric matrix; the use of polymeric systems for the synthesis of nanoparticles; preparation of liquid-crystalline polymers. Polymeric semiconductors possessing novel in principle structural properties and high electroconducting characteristics have been prepared by radiation-induced template gas-phase copolymerisation on extended polyamide films. Compounds that both manifest catalytic activity in polycyclotrimerisation of diisocyanates and behave as dyes have also been obtained. Other achievements include the development of an environmentally safe method for the synthesis and modification of polymers in supercritical media and synthesis of self-assembling hydrophobised ternary copolymers (terpolymers) by micellar polymerisation in aqueous solutions.

Many important discoveries made by researchers of INEOS have won international recognition. These include the first synthesis of carboranes and their numerous analogues, which represent a novel class of cage boron derivatives (L I Zakharkin, 1963); synthesis and analysis of carbyne, the third form of carbon (V V Korshak and A M Sladkov, 1971); theoretical prediction of fullerene C_{60}, the fourth form of carbon (D A Bochvar and E G Gal'pern, 1973) and discovery of a 1,2-rearrangement of polyhaloaliphatic radicals in the liquid phase (A N Nesmeyanov and R Kh Freidlina, 1973). Such important achievements as chemical fixation of molecular nitrogen and other small molecules under mild conditions (M E Vol'pin and V B Shur, 1967) and ionic hydrogenation (D N Kursanov, 1979) have acquired worldwide recognition. The discovery of an ability of achiral molecular structures to recognise enantiomers (V A Davankov and S V Rogozhin, 1992) has stimulated the development of ligand-exchange chromatography. And, last but not least, cyclic migration of unpaired electrons through polyvalent atoms of non-transition elements is yet another important discovery made in the mid-1990's (M I Kabachnik).

The priority in the development of 'synthetic food', of 'synthetic caviar' in particular also goes to INEOS. The idea of A N Nesmeyanov to introduce advanced chemical technology for the conversion of irrationally utilised natural proteins into a foodstuff has been realised in the production of synthetic caviar. Implementation of this process has been carried out by researchers of INEOS headed by S V Rogozhin and G L Slonimsky.

The staff of INEOS exceeds 550 researchers including 5 Full Members and Corresponding Members of the RAS, 78 Doctors of Science and 262 Ph.Ds. The Institute has in its structure 58 laboratories and research teams. About 2000 publications and 13 monographs summarise the achievements of INEOS over the past 5 years. The Institute collaborates with more than 150 universities, institutes and industrial centres both in Russia and abroad. It takes an active part in organization of diverse conferences, symposia and seminars, primarily those in the field of organometallic and organoelement chemistry. Among them are 'Chemistry of Organophosphorus Compounds' (1998), 'Horizons of Organic and Organometallic Chemistry' (1999), 'IMEBORON-XI' (2002), 'New Trends in Organometallic Chemistry and Catalysis' (to mark the 80th birthday of M E Vol'pin, 2003).

Some of the papers published in this issue reflect the main trends of research carried out at the Institute.

The review by A Z Kreindlin and M A Rybinskaya 'Cationic and neutral transition metal complexes with a tetramethylfulvene or trimethylallyldiene ligand' is devoted to systematisation of the published data on the synthesis, chemical properties and structures of transition metal complexes with tetramethylfulvene and trimethylallyldiene ligands formed from the respective precursor compounds (cyclopentadienyl complexes of these metals) upon thermolysis, photolysis, redox conversions and reactions with strong bases. A quantum-chemical description of the structures of these complexes has been given.

The review by V I Bregadze, S V Timofeev, I B Sivaev, I A Lobanova 'Substitution reactions at boron atoms in metallacarboranes' is a survey of the published data on substitution reactions in 10–12-apical metallacarboranes, which are being studied especially intensively. Special emphasis is laid on putative reaction mechanisms and effects of the metal fragment on the substitution site in the polyhedron.

The results of structural investigations of fullerene derivatives using diffraction methods are considered in the review by I S Neretin and Yu L Slovokhotov 'Crystal chemistry of fullerenes' which deals with an analysis of peculiarities of crystal structures of this type of compounds. This review presents the first generalisation of molecular and crystal structures of this group of compounds, which is one of the most difficult objects for investigation by diffraction methods.

The review by S V Vinogradova and V A Vasnev 'Trends in the development of polycondensation and condensation polymers' is an overview of progress in the polycondensation procedures. It provides a detailed description of the main principles of macromolecular design of condensation polymers and of some novel types of condensation polymers.

The review by L M Bronstein, S N Sidorov, P M Valetsky 'Nanostructured polymeric systems as nanoreactors for nanoparticle formation' gives a detailed description of the methods for the preparation of polymeric nanocomposites containing nanoparticles (block copolymers, dendrimers, nanoporous polymers, polyelectrolyte gel-surfactant complexes, multilayer films prepared by application of oppositely charged polyelectrolytes, *etc*.). Properties of nanostructurised polymeric nanocomposite materials are described.

The limited size of the issue prevents comprehensive presentation of the main research lines of the Institute.

All those who are interested in more detailed information about the Institute are invited to visit our web-site: http://www.ineos.ac.ru

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Director of INEOS RAS