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N. N. Semenov and the chemistry of the 20th century (to 100th anniversary of his birth)

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Abstract: The contribution of N.N. Semenov to the chemistry of the 20th century is described including his discovery of branching chain reactions and the development of the general theory of chain reactions and thermal explosions. Particular emphasis is made on his early understanding of the necessery to introduce modern physical concepts into new chemistry as well as his prediction that biology is likely to play a crucial role in the future chemistry.

Introduction.

N.N. Semenov got his Nobel Prize for Chemistry in 1956 jointly with Sir C.N. Hinshelwood for their researches into the mechanism of chemical reactions.
Semenov's most well-known contribution to chemistry was the discovery of the branching chain reactions and the development of the general theory of chain reactions. His book "Chain Reactions" published in 1934 in Leningrad (Russia)(ref. 1a) and the next year in Oxford (England)(ref. 1b) made a great impact on the minds of chemists, demonstrating the importance of chain reactions in chemistry and possibility of physical approach to the understanding of these complicated processes.
No doubt, these achievements as well as their subsequent development are of great importance for chemistry of the 20th century. Moreover the subsequent discovery of nuclear chain reactions could be regarded as the development of Semenov's ideas, this time in the field of nuclear physics. There is an evidence that already in 1933, actually immediately after he became acquainted with the discovery of neutron, Semenov predicted that neutrons could be used to propagate and branch nuclear chain reactions*.
One of Semenov's pupils and colleagues, Prof. Yu.B. Khariton, recalls that "N.N. used to virtually seize people to pull them to the blackboard in order to explain how to use the Fermi's discoveries of nuclear reactions under the influence of the neutrons."(ref. 2)
Nevertheless, these achievements, important as they are, are far from to cover all the Semenov's contribution to the science of the 20th century, even taking into account his prophecy on the possibility of nuclear chain reactions. I would like to emphasize in this article that he was one of the first scientists in the beginning of the 20th century who very clearly realized the crucial role of physics in the chemistry in the next decades and himself has made an important contribution to the development of a physical approach to chemical problems, which became a special branch of chemistry and which has greatly enriched chemical science. Moreover in the last period of his creative life he made a conclusion about great role of biology in the future chemistry and influenced much the development of the chemical physical approach to the biological and other molecularly organized chemical systems.

The origin.

N.N. mentioned several times that already in his youth he was interested in chemistry but then realized that physics was likely to play a very important role in the development of chemistry in the 20th century and, therefore, decided to study physics to be able to apply physical approach to the chemical science.
In this connection he paid tribute to two his "indirect teachers", J.H. Van't Hoff and S. Arrhenius, "whose books have made me to study physics with a special purpose to learn to apply it to chemical

* Professor S.P. Kapitza told us recently about this at press-conference citing his father, late Professor P.L. Kapitza, who was close friend of N.N. Semenov. Apparently this Semenov's prediction, (as well as many others) has not been published.

problems"(ref. 1) What books did he have in mind? The first was the Arrhenius book "Theories of Chemistry" published in 1906 in Sweden and made on the base of lectures in California. The book was translated into Russian in 1907.(ref. 3) "One of the Arrhenius books, "Theory of Chemistry",- recalled N.N.,- was bought by me when I was 15 and played an essential role in my life."(ref. 4)

The other book was Van't-Hoff "Etudes de Dynamique Chimique" published in Holland in French in 1884.(ref. 5) This second book was read by Semenov for the first time in Russian translation when he was preparing his "Chain Reactions", i.e. in the very end of the twenties or even in the beginning of the thirties. It is then that the Van't-Hoff book was translated into Russian by a colleague of Semenov, Prof. Blokh. At that time the direction of Semenov's work, the kinetics and mechanism of chemical reactions, was already formed.* While reading the Van't-Hoff book N.N. was fascinated by the profundity and boldness of the kinetic investigations of the author who was very much ahead of his time, and N.N. felt himself as Van't-Hoff's immediate follower. Apparently the book has made stronger the Semenov's decision to accomplish his "shift" to chemistry which had started earlier.

Hence, actually it was the Arrhenius book which played the decisive role. From the words of N.N. quoted above it could be concluded that at the age of 15 he merely followed the advice given by Arrhenius in his book. I decided to search for this advice in the book, but to my surprise I could not find anything like this. Rather on the contrary, in his book Arrhenius assures the readers that new theories in chemistry must be created only on the base of the previous chemical theories. In the foreword to his book he writes: "There are many who believe that the most modern scientific data are the more valuable, the less they depend on the previous theories in the field of chemistry. I believe that this is not correct. The fact that the new theoretical data have raised at the base of previous generally accepted ideas, gives the pledge for their truth. In my "Theories in Chemistry" I shall try to show that the newest parts of theoretical chemistry are logical and necessary deduction from the previous teaching along the way the chemistry as a precise science moved ahead during the last century."**

Thus Semenov himself has made the conclusion about the role of physics in the future of chemistry from the Arrhenius book. If to remember that Arrhenius wrote his book on the eve of ground-breaking experiments of Rutherford and appearance of the Bohr theory of the interatomic structure it will be clear that young Semenov possessed a remarkable intuition. Nevertheless, it must not necessarily be thought that N.N. saw the future better than Arrhenius, the author of the book. The thing is that chemical physics united both physics and chemistry, and the new theories, which appeared after the Arrhenius book was published, belonged actually to both physics and chemistry. For example, the Bohr theory gave the first theoretical base to the Mendeleev Periodic Table, which was naturally purely chemical invention. We have the evidence that N.N. continued to be interested in chemistry having decided to study physics at the Petrograd University after reading the "Theories in Chemistry".*** In 1918 the revolution brought Semenov to Siberian town Tomsk where in 1918-1920 he was teaching in the Tomsk University and the Technological Institute. There he organized a scientific seminar and at the beginning distributed a questionnaire among all teachers and students taking part in the seminar. Now we have a sheet of the questionnaire in our possession written of course by hand with his own answers to two questions (thank to late Professor Khodasevich of the Tomsk University who kept it for a very long time in Tomsk and then recently sent it to me). Here they are:

What report you would like to present yourself at the seminar?

Theory of quanta.

What problems (themes) do you consider desirable to enlighten at the Saturday meetings?

1) Werner theory of complex compounds. 2) About solvates.

It is seen from the Semenov's answers that being already physicist he was interested by purely chemical problems which were up to date not only in those old times.

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* I have a very good evidence that N.N. had not read the Van't-Hoff's book before 1929, and this evidence is not only based his poor knowledge of foreign languages. In 1929 Semenov book entitled "Modern Teaching of the Rates of Gaseous Chemical Reactions" was published, in which the name of Van't-Hoff *was not even mentioned.*[6] Naturally N.N. knew the Van't-Hoff's works (e. g. they are quoted in the book (ref. 7) published in 1927), but apparently from another literature.

** Translation into English from Russian version of the book.

*** I confess that initially I had some doubts about the planned destiny with the change from chemistry to physics and then back to chemistry.

It was of importance that as a physicist he started his work under supervision of outstanding scientist, Professor A.F. Ioffe, whose physical school became probably the most advanced in the young Soviet science. A.F. Ioffe fully supported the Semenov's desire to apply his knowledge in physics to chemical problems and shared his views about the role of physics in the 20th century chemistry.*

Chain reactions and chemical dynamics.

The discovery of branching chain reactions was made in Semenov's laboratory in 1925 in the Petrograd Physical Technical Institute directed by A.F. Ioffe. As every discovery this one happened unexpectedly when oxidation of phosphorous vapor was studied. Soon it was shown that the oxidation of molecular hydrogen, one of the simplest reactions from the viewpoint of its stoichiometry, is also a branching chain reaction with rather complicated mechanism including quite a few steps. Earlier Bodenstein in Germany postulated a chain mechanism for chlorination of hydrogen; the reaction became a classic example of the unbranched chain mechanism. Later it became clear that bromination of hydrogen, chlorination and bromination of various organic compounds, polymerization, cracking, many other reactions are actually chain reactions. To this category belong also multiple oxidation reactions with molecular oxygen as an oxidant both in gas and in liquid phases, which turned out also to be branching chain reactions, the branching being not so fast as in the oxidation of hydrogen, but usually rather slow. (According to Semenov this was called "degenerated branching"). Thus at close analysis both simple and complex (with respect to their stoichiometry) reactions turned out to be chain reactions, often branching chain reactions. Considering these facts and trying to make generalizations for his book "Chain Reactions" N.N. came to the conclusion that this is what one should expect as a consequence of fundamental physical laws regulating chemical processes. Indeed the molecules themselves do not react with each other easily even at sufficiently high temperatures. E.g. one can keep the mixture of oxygen and hydrogen, as long as one wants without any interaction, in a vessel under the conditions of temperature and pressure outside of the explosion limits.**

At the same time atoms and radicals react with molecules with fast rates. Inside of the "explosion peninsula", even when initiation is extremely slow, the reaction looks as an explosion: so fast is the reaction rate of molecules with atoms and free radicals (at the transfer through the explosion limits the chain length may be regarded as increasing to the infinity, and the concentration of active particles grows dramatically.) At the interaction of an atom or a radical with a molecule the number of electrons remains uneven, i.e. a new radical appears necessarily, hence a chain must inevitably arise. If the energy evolved in the elementary reaction of a radical with a molecule is sufficiently large, this energy can be used to cleave one more bond, additional radicals will be born and, therefore, chain branching will take place. Other ways to perform a chemical reaction are simply not envisaged. N.N. Semenov made the conclusion in 1934 that "great majority of reactions at close look are chain reactions".

These considerations looked sufficiently convincing (at that time) only for gas phase reactions, since ions were known to exist in polar solutions. But ions can also start a chain of transformations (in this case the charge plays the role similar to that of unshared electron in free radical). There are also important reactions of heterogeneous catalysis which attracted great interest of N.N. Semenov since very long ago. But at the surface of a catalyst (e.g. metal or metal oxide) chains may be originated too. Thus, the theory

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* A.F. Ioffe wrote an interesting foreword to the book written by Semenov and his very young pupils and co-authors (V.N. Kondratiev and Yu.B. Khariton) "Electronic Chemistry", (1927). (ref. 7) Presumably under the influence of N.N. his teacher writes the following in particular in this foreword: "It became clear from the very beginning of the appearance of the Bohr theory of the atomic structure, that it will be the base not only for spectroscopy...but for all the chemistry in general <...>. Moreover all the results of the Werner theory covering are consistent with the Bohr atomic theory. (Note that the Werner theory is mentioned again - A. Sh.) We are now at the very start of this new stream in chemistry so tightly bound to physics. <...> New thinking must combine with the ideas based on the chemical experience. As the result of their synthesis a new chemistry will perhaps grow..."

** Branching chain reactions are characterized by limit phenomena, e. g. with respect to pressure and temperature. There can be two or even three pressure limits. Under lower limit and above the upper one the reaction is virtually unobservable while inside of so called "explosion peninsula" proceeds as self inflammation. N.N. Semenov found a simple explanation for these exciting phenomena. If there is a chain branching the reaction rate is determined by the relative rates of chain termination and branching. When the termination is faster than the branching the reaction can proceed with negligible rate (if the initiation is slow), whereas when the branching is faster than termination the reaction proceeds as an explosion of chain reactions looked as the theory of all or at least "great majority" of chemical reactions. It was natural, therefore, to inspire almost all scientists of the Institute of Chemical Physics, which had just been created by N.N. in Leningrad (1931), to study the problems of chain reactions, the more so as the number of scientists working in the Institute was initially very small.

Simultaneously N.N. Semenov and his colleagues were developing the theory of thermal explosion and the theory of combustion. These investigations turned out to be very useful during the war with Germany (1941-1945). The Institute of Chemical Physics was evacuated to Kazan and continued to function there during the war helping to the military efforts of the state. To the end of the war the Institute was transferred to Moscow (1944) and the work on chain reactions were continued successfully at the new site.

Already in the sixties I and my colleagues made some contribution to the development of the field of chain reactions. Most interesting turned out to be the discovery of branching through the exited molecules in fluorination of hydrogen as well as of many organic compounds. In elementary steps of chain fluorination much energy is evolved as a rule which is often sufficient to break the weakest bond of the molecule formed. Initially the large part of energy is accumulated in the excited molecule and if the molecule decomposes to form atoms or radicals before loosing this energy, the chain is branching. Even if the energy is not sufficient for unimolecular decomposition, the atoms and radicals can be originated in a bimolecular reaction of the excited molecule with the fluorine molecule. E. g. in fluorination of hydrogen the propagation of the chain involves the reactions:

$$F\cdot + H_2 \rightarrow FH + H\cdot$$
$$H\cdot + F_2 \rightarrow HF^* + F\cdot$$

the HF molecule is sufficiently excited to break down the F-F bond. This results in branching, which manifests itself in typical phenomena of temperature and pressure limits.*

As was mentioned above initially (in the twenties) Semenov considered the branching through the formation of excited molecules typical for chain reactions. Later in the reaction of hydrogen with oxygen the conclusion was made that the branching proceeds along the following reactions:

$$H\cdot + O_2 \rightarrow HO\cdot + \cdot O\cdot$$
$$\cdot O\cdot + H_2 \rightarrow \cdot OH + H\cdot$$

In this mechanism excited particles do not seem to play part.**

This example was considered as classic case of branching and it was decided that branching does not involve excited states. Discovery of branching chain reactions for fluorination confirmed Semenov's initial ideas about the role of excited molecules, and fluorination area was found to be very fruitful for checking different conclusions of Semenov's theoretical predictions, since branchings turned out to be typical for gas phase fluorination.

In this article it is impossible to give any detailed review of chain reactions in chemistry. To confirm the conclusion about their importance I shall restrict myself to the quotation from a modern book written by Prof. D. Astruc (France) and published in 1995.(ref. 8) D. Astruc describes the chain reactions in organometallic chemistry in solutions. He writes the following in particular in conclusion to one of the chapters:

"The design of chain reactions is an example of engineering of chemical reactions using electron or atom transfer. It requires the knowledge of oxidation and reduction potentials or of metal-atom bond strengths of the substrates and products. It is a powerful way to overcome kinetic barriers by providing a rate increase of the order of 10^9 with the use of catalytic amounts of electrons or electron holes, of light or of a redox reagent. This area has been quite successful in organic chemistry, but even more so for inorganic and organometallic reactions due to the ability of transition metals to change their oxidation states. The chain mechanism has proven efficient for most inorganic and organometallic reactions of mono- and polynuclear systems: ligand exchange including chelation and

* According to the experimental data HF^* initially transfers the part of its excitation energy to molecular hydrogen which in its turn reacts with F_2 according to the scheme:

$$H^*_2 + F_2 \rightarrow H\cdot + HF + F\cdot$$

** In fact the reaction $H\cdot + O_2 \rightarrow HO\cdot + \cdot O\cdot$ may be regarded as involving extremely short-lived excited radical: $H\cdot + O_2 \rightarrow [HO^*_2] \rightarrow HO\cdot + \cdot O\cdot$.

decomplexation, isomerization, disproportionation, migratory insertion, and extrusion, oxidative addition, and reductive elimination. Electron and atom-transfer-chain reactions have even been extended to group-transfer-chain reactions in a few cases. Perhaps the most promising potential for this area is the coupling of chain reactions with organometallic catalysis, the pioneering example of which being the polymerization of terminal alkynes. Another challenging area is the disclosure of chain reactions of bioinorgahic complexes in biological systems".

The words: "The chain mechanism has proven efficient for *most* inorganic and organometallic reactions" are not far from the Semenov's prophecy of 1934 that *the majority* of reactions are chain reactions.

It is clear that Semenov of the middle of fifties wreathed with laurels of the Nobel prize could quietly continue his works together with his colleagues developing the area of chain reactions and feeling satisfaction in the fact that his ideas of the theories found lots of confirmations at the end of the century.

Nevertheless it was not natural for Semenov to rest content with what has been achieved however important these achievements were.

Chemical physics is broader than the area of chain reactions

I met N.N. Semenov in 1952 in Kiev and soon following his invitation became his post-gradient student in the Moscow Institute of Chemical Physics.

To this time the chain theory has triumphed in all its aspects. In particular bold Semenov's conclusions were confirmed remarkably well concerning great concentrations of atoms and free radicals formed inside the explosion limits in oxidation of hydrogen and others substances, many other conclusions of chain theory were also confirmed. It was already known that two types of ignition: chain and thermal, discovered and described by Semenov in chemical systems were found later also for nuclear reactions. It could be mentioned that N.N. Semenov and his colleagues were involved in creation of atomic weapons in USSR.

Soon, however, N.N. fully returned to the problems of his main interest: kinetics and mechanism of chemical reactions. The Institute continued to study chain reactions of thermal decomposition, oxidation, chlorination etc. However in the middle of fifties Semenov comes to the conclusion that chain reactions are far from to be the only way of chemical transformations. Unexpectedly for all of us just in the time of his triumph he started to express his deep dissatisfaction with the area of research of the scientists of his Institute. In his statements of that time directed to his colleagues he requires to search for new problems, to reject the accepted stereotypes, to put forward new ideas. In one of his addresses he even claimed that the chain theory is virtually completed, and there is nothing of principal importance to be found in this area. This was of course an erroneous conclusion (as we have seen above) but this error is quite understandable. I believe that he himself clearly realized that in fact the area of chain reactions continued to expand and had still many interesting problems to solve. Chain reactions remained the dearest field to his heart during all his life. It is not accidental of course that when he recreated his laboratory in the Institute (in 1971) he called it the laboratory of chain processes and, although being already 75 years old, took an active part in the investigations.

But the main concern of Semenov was the danger that the Institute he created would restrict itself by the framework of the problems once developed successfully by himself. Several times I heard his apprehensions based on the observations of many well-known schools of science. A prominent scientist starts a new direction which is very progressive at the beginning but later his followers continue to develop this area of science even when the area is virtually exhausted. In this way the field which once was very important and fruitful degenerates in the study of nonimportant details but continues to be sanctified by the name of the founder. Meantime the chemical physics which according to N.N. Semenov is the investigation of the physical essence of chemical processes must be the theoretical base of the *whole* of chemistry. It will be alive until the chemistry continues to live. To this time N.N. Semenov realized that however important is the area of chain reactions it is far to cover the entire chemistry. It became clear that the majority of ionic reactions in solution, many reactions of heterogeneous and homogeneous catalysis, e. g. those involving metal complexes often do not involve chains. Many purely molecular reactions do exist as well. That is why N.N. Semenov started to persuade his pupils, particularly young ones, to drastically change the field of their research. New areas of research were originated at that time in the Institute of Chemical Physics, such as quantum effects in reactions at low temperature, electroconductivity and superconductivity of organic materials, homogeneous catalysis by metal complexes etc.

He attracted many people to the problems connected with biology.

To learn from the living nature.

Thus in the fifties quite a few young scientists of the Semenov Institute sharply changed the direction of their research with full support and approval of the director.*

I shall briefly describe here only one new field which is close to me personally. From studying the gas phase reaction kinetics. I shifted to a new (at that time) field of catalysis with metal complexes and then further to the search and investigation of analogues of enzymes, catalysts of biological systems. For a long time chemists have been fascinated by some peculiarities of enzymes such as of very high efficiency, selectivity, capability to catalyze the reactions unknown in "usual" chemistry. The attempts to mimick enzymes started long ago but initially did not lead to a great success. Nowadays the situation has been essentially changed. First of all the mechanism of the enzyme functioning which was largely enigmatic earlier is now much more clear. At present we know the main types of chemical elementary processes and can apply chemical-physical approach to build catalytic systems. The problem is to create much simpler but almost similarly effective and more stable catalysts using the principles of biologic catalysis. This area is one of the possible approaches to the general problem to use the principles of biological organization in order to create chemical systems of the new types. It is this field, now called biomimetics, which became one of the strongest animations of N.N. Semenov in the last years of his life. Many times he stressed that the chemistry of the future must learn the ways which were developed as the result of the long evolution in living nature. It is in this way that we may create effective, energy saving, ecologically pure processes characteristic for the living nature. Evidently under the influence of N.N. this field of research became most interesting also for me.

For our research we have chosen the processes which play important role in living nature but were unknown in "usual" chemistry until recently: nitrogen fixation, methane oxidation at low temperatures, photosynthesis. Biomimetics is very fruitful field when it is combined with chemical-physical approach. It is deep understanding of the physical essence of the process that helps to build the simple analogues of enzymes without trying to copy all their details. In our work we have got a convincing evidence of fruitfulness of such an approach. Having created rather simple systems we managed to carry out new reactions unknown before in chemistry (for details see the reviews.(ref. 9, 10)

Each successful step in this direction excited great interest of Semenov and strengthened his enthusiasm. According to my observations even the discovery of chain reactions with branching through excited molecules, mentioned above which confirmed his own hypothesis put forward in the twenties was not met with such a pleasure as the information that now we can efficiently reduce molecular nitrogen to produce hydrazine or ammonia in water or alcohol under atmospheric pressure and at room temperature.

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* In order to encourage those who hesitated to make up their minds to change their field of research N.N. used to say that a scientist who has just started to work at a new and unknown problem may be compared with young fencer who is a beginner but starts the fight with an experienced master of fencing. It is the beginner who may win since the experienced fencer is prepared to repulse a standart blow, but without full knowledge of all the rules the beginner may deliver a sudden blow which is not expected by the experienced master.

I would like to stress again that N.N. Semenov was the author and consistent realizator of a new methodology based on the study of physical essence of chemical transformations. This methodology allows to develop a full understanding of the reactions mechanism and then to choose an optimal technology of a catalytic synthesis or to discover a new reaction. The most outstanding achievements in chemical science and practice are to be expected in the interdisciplinary research based on the combined use of the principles of the living nature, understanding of the physics of the chemical process under investigation and bold experiments with the help of chemical intuition. It is in the deep understanding of the great role of physics and biology for the present and the future chemistry that I see particularly important contribution of Semenov to the chemical science and taking into account his own achievements, it allows to pay tribute to him as a great scientist who was much ahead of his own time.

References.

1a. N.N. Semenov, *Chain Reactions*, ONTI, Leningrad, (1934), (russ.)

1b. N.N. Semenov, *Chemical Kinetics and Chain Reactions*, Oxford University Press, London, (1935).

2. Yu.B. Khariton, in: *Memoirs about Academician Semenov*, Nauka, Moscow, (1993), p. 30, (russ.)

3. S. Arrhenius, *Theories of Chemistry*, St. Petersburg, (1907), (russ.)

4. N.N. Semenov, *Science and Society*, 2nd Ed., Nauka, Moscow, (1981), p. 410 (russ.)

5. J.H. Van't-Hoff, *Etudes de Dynamique chimique*, Muller&Co, Amsterdam, (1884).

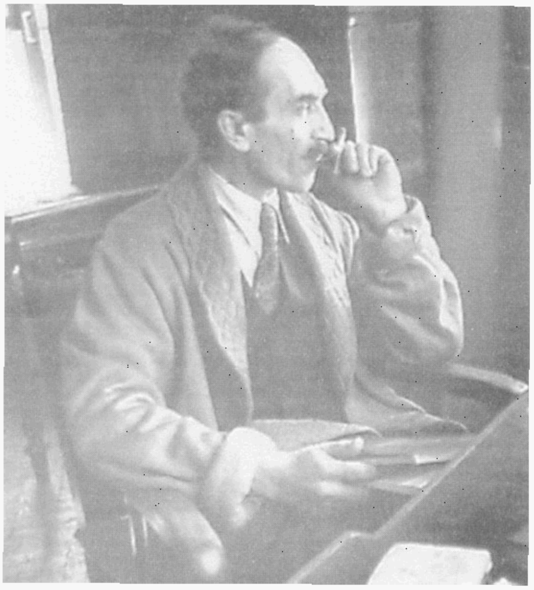
6. N.N. Semenov, *Modern Teaching on the Rates of Gaseous Chemical Reactions*, Gosizdat, Moscow - Leningrad, (1929), (russ.)

7. V.N. Kondratiev, N.N. Semenov, Yu.B. Khariton, *Electronic Chemistry*, Gosizdat, Moscow - Leningrad, (1927), (russ.)

8. D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, VCH, New York, (1995), p. 470.

9. A.E. Shilov in: *Perspectives in Catalysis*, J.M. Thomas, K.I. Zamaraev, Eds., Blackwell Scientific Publications, Oxford, (1992), p. 169.

10. T.A. Bazhenova, A.E. Shilov, *Coord. Chem. Rev.*, **144**, 69, (1995).



N. N. Semenov