

Alexander Abramovich Grinberg

RESEARCH ON THE CO-ORDINATION COMPOUNDS OF THE PLATINUM METALS

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This year marks the twentieth anniversary of the death of Academician A. A. Grinberg who, fifty years ago, founded a new field of science to study the chemistry of co-ordination compounds of the platinum metals at the Lensoviet Institute of Technology in Leningrad. His academic life was devoted to this subject and his many contributions continue to form a source of inspiration to his successors.

Alexander Abramovich Grinberg (1-5), a full member of the U.S.S.R. Academy of Sciences, was born in St. Petersburg on 2nd May 1898. After graduating from the Gymnasium with a gold medal in 1916, he entered the Physico-Mathematical Faculty of the Petrograd State University to join the medical group. Later he moved to the chemistry department of the same faculty. In those times, the university professors included such distinguished chemists as

A. E. Favorsky, L. A. Chugaev, V. N. Ipatiev, M. S. Vrevsky, V. E. Tishchenko, Yu. S. Zalkind, and S. V. Lebedev. This fact of his transfer from the medical group to the department of chemistry was later used by his friends to make jokes to the effect that "the chemists had stolen Alexander Abramovich from medicine".

Grinberg finished at the university in 1924, while in 1920 he began his work at an institute founded by L. A. Chugaev to study platinum and the other noble metals. Late in the nineteenth and early in the twentieth century Russia was the main supplier of platinum to the world market from the rich platinum deposits discovered in the Urals in 1822. Thus, platinum and its satellites were one of the riches of Russia, and it was of course necessary to study these riches. Immediately after the Great



Alexander Abramovich Grinberg 1898-1966

A full Member of the U.S.S.R. Academy of Sciences and Head of the Chair of General and Inorganic Chemistry at the Lensoviet Institute of Technology in Leningrad, Grinberg developed the theory of co-ordination chemistry on the basis of platinum metal compounds. His enthusiasm was to influence many of his former students to devote their academic careers to the study of co-ordination chemistry in general and the chemistry of the platinum metals in particular, as he had done

October Revolution of 1917, in those difficult times for the newly born nation, the young government of Soviet Russia made a decision to establish a network of scientific research institutes and among the first research establishments founded in April 1918 was the Institute for Platinum Studies.

A. A. Grinberg began working in this institute almost from its start-up and he continued there until 1934 when the institute was transferred to Moscow to become the main core of the Institute of General and Inorganic Chemistry of the U.S.S.R. Academy of Sciences.

The chemistry of platinum metal compounds is essentially that of their co-ordination compounds, and the theory that correctly described the main features of their structure was presented by Alfred Werner as far back as 1893. This theory was by no means accepted immediately by all chemists, and critical comments continued until the 1930s. L. A. Chugaev was quick, however, to recognise the advantages of Werner's theory, and he adopted it as a guiding principle in the research activities on the Group VIII elements of the Periodic System and above all platinum metals, and he is rightly considered to be the father of Soviet co-ordination chemistry. Outstanding contributions to the chemistry of co-ordination compounds were made by the pupils of L. A. Chugaev and by his associates in the Institute of Platinum, such as I. I. Chernyaev, V. G. Khlopin, N. K. Pshenitsyn, V. V. Lebedinsky, E. Kh. Fritsman, and many others. Among these, an important part was played by A. A. Grinberg.

Grinberg started his pedagogical activities in 1928 when he became an assistant professor and then *privatdocent*, while from 1932 he became Professor of General and Inorganic Chemistry at the I. P. Pavlov Institute of Medicine in Leningrad. From 1936 he held the Chair of General and Inorganic Chemistry at the Lensoviet Institute of Technology. There Grinberg created a large scientific school of his own which produced many of the leading Soviet specialists in co-ordination chemistry and in the chemistry of platinum metals. His broad interests in science,

combined with his enthusiasm and friendliness, drew associates and students closer to him, and under the influence of his bright personality many of the graduates from the Lensoviet Institute of Technology devoted their life to co-ordination chemistry and to the chemistry of the platinum metals. It was here that he wrote the textbook "Introduction to the Chemistry of Complex Compounds", which was published four times and translated into many languages. For several decades this was a standard text for large numbers of students, post-graduates, institute teachers and research associates. Additionally, in 1936, he edited the Russian translation of A. Werner's "New Ideas in the Field of Inorganic Chemistry", published in the Soviet Union. (One of the two translators of this book was A. A. Grinberg's mother, Yekaterina Mikhailovna.)

During World War II Grinberg was evacuated with the Institute of Technology from Leningrad to the town of Kazan. There he worked shoulder to shoulder with A. E. Arbuzov, an outstanding researcher of organic phosphorus compounds, and the joint activities of these two men of science in Kazan resulted in the establishment of a laboratory to study the complex compounds of platinum metals with organic phosphorus ligands. This laboratory still remains very active.

In Kazan, Grinberg became Head of the Laboratory at the Institute of Radium which had also been evacuated from Leningrad. Cooperation with this institute, however, had begun in Leningrad several years before just after the first European cyclotron was commissioned there in 1936. Already in the pre-war years, Grinberg, together with F. M. Filinov, used the cyclotron to obtain radioactive isotopes of platinum, iridium and bromine which were utilised in the study of co-ordination compounds. Grinberg headed this laboratory in the Institute of Radium until his death.

In 1943 Grinberg was elected Corresponding Member, and in 1958 Full Member, of the U.S.S.R. Academy of Sciences, while for his contribution to science and for his scientific

organisation activities, he was awarded many high government honours, including one Order of Lenin, one Order of the Red Banner of Labour and an Order of the Red Star. He was also given the title of Worker Emeritus of Science and Technology.

Grinberg's Publications

The first papers written by A. A. Grinberg on research in the co-ordination compounds of platinum concerned stereochemistry. At this time opponents of Werner's co-ordination theory were doing their utmost to invalidate the square-planar structure of platinum(II) complexes. Such publications were written, in particular, by Reilen and Nestle (6) in the late 1920s and also by Drew and co-workers in the early 1930s (7). On the basis of the measurement of molecular weights of Peyrone's chloride ($\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$) and of Reise's second base chloride ($\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$) in liquid ammonia, Reilen and Nestle arrived at the conclusion that the latter complex was essentially a dimer and, consequently, the two complexes were not isomers. However, Grinberg synthesised isomeric $[\text{Pt}(\text{NH}_3)_2(\text{SCN})_2]$ complexes and measured their molecular weights in acetone (8). These happened to be equal, which confirmed that the complexes were isomeric. If complexes of this composition were isomeric they must have a square-planar structure, which supported Werner's theory.

Also of importance was Grinberg's research using ligands which form chelate rings, such as $\text{C}_2\text{O}_4^{2-}$, $\text{NH}_2\text{CH}_2\text{COO}^-$, to determine the geometric configuration of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complexes (9). For example, when interacted with oxalic acid and glycine, the $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complex forms $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$ and $[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{CH}_2\text{COO})]^+$, respectively, while $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ leads to the formation of $\text{trans-}[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4\text{H})_2]$ and $\text{trans-}[\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{CH}_2\text{COOH})_2]^{2+}$. In other words, one mole of the ligand reacts with one mole of the complex in the first case, and two moles react in the second, which was consistent with the proposed isomeric structures.

In addition the successful synthesis of the

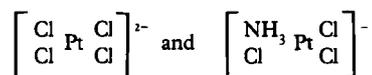
cis-trans- isomeric glycine compounds $[\text{Pt Gl}_2]$, where $(\text{Gl}=\text{NH}_2\text{CH}_2\text{COO}^-)$, (10) can be related to the research in stereochemistry and testified to the square-planar structure of the given complexes. Attempts had been made before Grinberg's time to synthesise these isomeric complexes predicted by the co-ordination theory, but without success.

In the late 1920s and early 1930s, many researchers were also attempting to synthesise the analogous isomeric complexes of palladium(II). One of the goals of such syntheses was to determine whether these complexes had a square-planar or a tetrahedral structure. Back in 1927, Krauss and Brodkord (11) reported that they had obtained isomeric complexes of the $[\text{PdA}_2\text{X}_2]$ type (where A=ammonia or organic amines). Grinberg (12) and Drew, Pinkard, Preston and Wardlaw (13) reproduced their data and arrived at the conclusion that they had obtained $[\text{PdA}_2\text{X}_2]$ and $[\text{PdA}_4]$ - $[\text{PdX}_4]$, but not isomeric compounds. Based on this, Drew and colleagues rejected the possibility that geometrical isomerism existed in the complexes of palladium(II). At the same time, Grinberg directed his efforts to obtain the missing isomer. Properties of palladium(II) complexes of the type $[\text{PdA}_2\text{X}_2]$ had been obtained by that time and these pointed to a trans-configuration. Utilising the method of synthesising the $\text{cis-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complex, Grinberg was fortunate and synthesised $\text{cis-}[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ (14), thus confirming the square-planar configuration of palladium(II) complexes.

One of the central problems of co-ordination chemistry has been, and to some extent still remains, the problem of the mutual influence of ligands, particularly on reactivity. In 1926 I. I. Chernyaev discovered the trans-influence phenomenon (15) which was later expressed in the form of a law (16). Throughout all of his activities in science, Grinberg was busy in research directed to the experimental and theoretical confirmation and development of this law. In 1932, simultaneously with B. V. Nekrasov, he explained the law of trans-influence using polarisation concepts. A later

development was a rather fruitful idea concerning the nature of the trans-influence, from the viewpoint of the oxidative and reductive properties of ligands (17).

In the first edition of his monograph, "Introduction to the Chemistry of Complex Compounds" (18), Grinberg wrote: "The law of trans-influence does not presuppose in any way that the interaction of trans-groups by way of a central metal atom is the only kind of interaction which is possible between co-ordinated groups combined in one complex nucleus. It is evident that groups in the cis-position also can (and must) cause an influence on one another." In the mid-1950s, Grinberg experimentally demonstrated the influence of ligands in the cis-position (19). This resulted from a study of the kinetics of reactions in which chloride ligands were substituted by ammonia in the complexes:



If the cis-positioned ligands did not influence one another, then the rate of substitution reactions on the co-ordinate Cl-Pt-Cl in these complexes should be very similar. However, the experimental data showed that the rate of substitution in the ion $[\text{PtNH}_3\text{Cl}_3]^{-}$ is higher than that in $[\text{PtCl}_4]^{2-}$. The same picture could be observed from the isotope exchange of chloride ligands. Later, Grinberg and his pupils studied analogous complexes with ligands such as pyridine, aliphatic amines, ethylene, thioethers and sulphoxides, instead of ammonia. In general the cis-influence of these ligands was found to be in the reversed sequence compared to their trans-influence (16). For example, ammonia has a small trans-influence value but has a relatively high cis-influence. In contrast, ethylene has a high trans-influence but a low cis-influence.

A. A. Grinberg was one of the first to have used radioactive isotopes in studies on co-ordination compounds. For example, he studied the isotope exchange of the bromide ligand in the complexes $[\text{PtBr}_4]^{2-}$ and $[\text{PtBr}_6]^{2-}$ and obtained important conclusions (20). He asserted that in spite of the high stability of

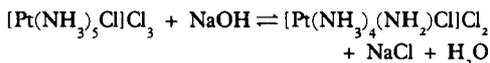
these complex ions, the ligands in their inner spheres were labile. Also important was the conclusion that all of the bromide ligands in each of the complexes in question happened to be of equal value. From this it followed that there was no difference whatsoever between the main and additional valencies.

Grinberg's investigations with the use of radioactive markers resulted in other very important conclusions. Suffice to say that using an example of the isotope exchange of ligands of the type $[\text{PtX}_4]^{2-}$ (where $\text{X} = \text{Cl}^{-}, \text{Br}^{-}, \text{I}^{-}, \text{CN}^{-}$), a seemingly paradoxical phenomenon was found: the thermodynamic stability of complexes did not agree with their kinetic lability. It appeared that the more stable the complex the faster the ligands exchanged therein. Later, a similar situation was disclosed by Hertz on type $[\text{HgX}_4]^{2-}$ mercury complexes (21). Grinberg, however, did not think that such behaviour for identical complexes of the same metal was widespread, and he warned other researchers against making too extensive generalisations.

Kinetic research into the substitution reactions and the isotope exchange of inner-sphere ligands made it possible for Grinberg to detect the mechanism of many of the reactions. His papers show the important role played by the solvent in these reactions. It has been found that in water solutions, many isotope exchange and alkaline hydrolysis reactions of the complex compounds of platinum(II) proceed via an initial aquation step, while in non-co-ordinating solvents exchange can be carried out by the direct substitution of ligands. The reaction mechanisms of isotope exchange and substitution in the octahedral complexes of platinum(IV) are more diversified. A substantial role in these reactions is played by the acid-base properties of the complexes, and redox mechanisms can be involved.

A great contribution was made by Grinberg towards the science of acid-base properties of co-ordination compounds. In his early research activities he showed that the following reaction, which produces an amidotetrammine complex and was first carried out by L. A.

Chugaev, involved a reversible change of spectrum in the ultraviolet region:



He also discovered that a similar change in the spectra of amine complexes of platinum(IV) influenced by an alkali could be observed in many instances, thereby demonstrating the deprotonation of the amine ligands. In this connection Grinberg put forward a supposition, later confirmed, that all of the co-ordination compounds of metals containing RH ligands were potentially acid in nature. Subsequent research activities of Grinberg and of his numerous pupils were associated with the quantitative characteristics of the acidic properties of amino- and aquo-complexes of different metals. After many years of research work, Grinberg formulated generalisations about the relationship of acidic properties of complexes and a number of factors: namely central metal charge, complex ion charge, the geometrical structure, the tendency of the free ligand towards acidic dissociation and other factors. These guidelines make it possible to predict the properties of yet unknown compounds (22).

A. A. Grinberg paid a large amount of attention to the study of red-ox properties of the

co-ordination compounds of platinum metals. Early in the 1930s he wrote a paper that established the possibility of quantitative oxidation of certain platinum(II) compounds using permanganate (23), and for many years this reaction had a significant place in analytical practice. For Grinberg it happened to be the beginning of a new direction in his research activities, that is the study of red-ox properties of co-ordination compounds. As a result of research in this direction, the influence of the nature of ligands upon a red-ox potential was disclosed, and an idea was formulated on the nature of phenomena defining the red-ox potential.

The exact nature of the nitrile-amine compounds of platinum(II) (24) were the subject of discussion among researchers for a long time. These were synthesised for the first time in 1915 (25) and remained an enigma until early in the 1960s. Back in 1950, in his important paper about the $[\text{Pt}(\text{NCCH}_3)_2(\text{NH}_3)_4]\text{Cl}_2$ complex, Sidgwick wrote that there should not have been any doubt that platinum in that compound has a covalence of 6. In 1951 Grinberg expressed an idea that the amino-nitrile complexes of platinum(II) were essentially compounds with intra-sphere amidines (27). Several years later, using infrared spectroscopy, Kharitonov was



A. A. Grinberg with one of his pupils and followers in research on the co-ordination chemistry of platinum metals, Professor Y. N. Kukushkin, the author of this paper, and the present Head of the Chair of General and Inorganic Chemistry at the Lensoviet Institute of Technology

able to confirm this supposition (28). It is known that the degree of conversion of alkyl-nitriles into amidines is not very high under ambient conditions (29). However, formation of amidines in the internal sphere of complexes becomes much easier as a consequence of their co-ordination. The effect of co-ordination on ligand reactivity continues to be a major research topic in co-ordination chemistry, particularly as it is directly related to metallo-complex catalysis.

In recent times bioinorganic chemistry has become an independent branch detached from co-ordination chemistry, and Grinberg also stood on the threshold of this field of science. Early in the 1950s, he suggested that M. A. Azizov should begin to study co-ordination compounds using biological compounds as ligands. Now, the laboratory of Professor Azizov is one of the leaders in the U.S.S.R. in the field of research and application of biologically active co-ordination compounds.

Grinberg devoted all his adult life to co-ordination chemistry in general and to the chemistry of platinum metals in particular. He left behind for his successors a large scientific inheritance, and the thoughts and ideas expressed in his papers and monographs still continue to be used by many researchers as a source of inspiration for further investigations.

A human death is always premature. A. A. Grinberg was caught by death during a period of great creativity. Until his last days he was busy preparing a report for the International Conference on Co-ordination Chemistry (I.C.C.C.) to be held in Geneva and devoted to the centenary of the birth of Alfred Werner, creator of the co-ordination theory.

Every year, early in May, in the Leningrad Institute of Technology in Leningrad, a ceremonial meeting is held at which the pupils and followers of Alexander Abramovich Grinberg read a lecture about this great scientist and remarkable man.

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