Aleksandr Abramovich Grinberg (1898–1966), Russian Coordination Chemist: A Centennial Retrospect

George B. Kauffman

Department of Chemistry, California State University, Fresno, Fresno, CA 93740-8034, george_kauffman@csufresno.edu

Abstract: This article is dedicated to the memory of Professor Yurii Nikolaevich Kukushkin (1931-1998), who died suddenly of a stroke on November 30, 1998, during its composition.

Everybody is aware of the fact that the combustion of kerosene produces not only CO_2 but also CO with possibly lethal consequences. The typical chemistry texts mention, of course, competing or consecutive reactions; however, in the section on stoichiometry and the balancing of reactions they invariably restrict the discussion to single reaction systems and ask the students to balance equations given in a skeletal form. The tacit implication is that every balancing problem has a unique solution. The students, and some teachers [1] as well, are then very surprised if they find a sizable number of equations for some chemical systems, all perfectly well-balanced, which are not just multiples of each other.

Aleksandr Abramovich Grinberg (1898–1966) (Figure 1) was one of Russia's most prominent and prolific authorities on the chemistry of the platinum group metals, particularly platinum. Inasmuch as most of the compounds of these elements are complexes, he thus became one of the world's leading coordination chemists. Because little information about him is available in English [1, 2], the present article is intended to acquaint chemists and historians who do not read Russian with the life and contributions of this talented and dedicated practitioner of our science (Figure 2).

My Grinberg Connection

I was recently asked to present a few words on Grinberg's contributions to coordination chemistry in the personal context of an American chemist on the occasion of the centennial celebration of his birth, held in St. Petersburg on May 14, 1998 [3]. These were translated into Russian by Yurii Sergeevich Varshavskii and read by the late Yurii Nikolaevich Kukushkin. They document the development of my interest in Russian chemists and chemistry in general and Grinberg in particular:

> From my early adolescence I have been an aficionado of Russian music and am still particularly fond of Chaikovskii, Rachmaninov, Shostakovich, Khatchaturian, and the group known in the West as "The Five" and in Russia as "The Mighty Little Heap" (*Moguchaia Kuchka*) (Balakirev, Borodin, Cui, Mussorgskii, and Rimskii-Korsakov). My musical and chemical interests coincided on the occasion of the Borodin centennial [4] when Charlene Steinberg and I collaborated in translating into English Nikolai Aleksandrovich Figurovskii and Yurii Ivanovich Solov'ev's 1950 biography of chemist-composer Aleksandr Porfir'evich Borodin [5].
>
> My interest in coordination chemistry and the history of Russian chemistry converged when, beginning with the late 1950s, my students and I carried out research on the column and thin-layer chromatographic separation and structural studies of geometrically isomeric coordination compounds on various adsorbents [6]. Because ideal isomer pairs for separation should be inert so as to minimize isomerization, we began our separations using coordination compounds of the platinum metals, especially platinum, iridium, rhodium, and palladium, among Russia's most important natural resources. Because much of the pioneering work on the platinum metals was carried out by Russian chemists, I directed my historical interests to a series of biographies of these men [7]. For these the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR awarded me its Chugaev, Kurnakov, and Chernyaev medals, which I treasure among my most cherished honors (Chugaev was Grinberg's mentor) (Figure 3).
>
> In 1969 the USSR Academy of Sciences also invited me to contribute two articles on relations between Dmitrii Ivanovich Mendeleev and American chemists to a special volume of *Voprosy Istorii Estestvoznaniia i Tekhniki* commemorating the centenary of the periodic system [8]. In 1971 I was asked to preside at a session of the 13th International Congress of the History of Science held that year in Moscow, where I met Boris Rosen, one of Grinberg's former students, who was to arrange for me to meet Grinberg's widow in Leningrad (now St. Petersburg). Because I was the only Western scientist to receive these two invitations, I felt particularly honored. Although my wife Laurie and I did visit Leningrad, unfortunately we were unable to meet Mrs. Grinberg (who died later on April 16, 1985), thus delaying my projected Grinberg biographical article.
>
> In the course of our work, my students and I developed reproducible syntheses for several dozen platinum metal complexes [9], including an isomer pair that played a prominent role the history of Werner's coordination theory [10] from its inception in 1893, namely, *cis*- and *trans*-diamminedichloroplatinum(II) (with Dwaine O. Cowan) [11], which the Institute for Scientific Information in 1987 designated as a "Citation Classic" __ "one of the most frequently cited works in its field" [12]. It was with such diammines of dipositive platinum that Grinberg [13] began his work on coordination chemistry in 1927 in order to prove the square planar configuration of platinum(II), which had been postulated by Werner in 1893 [10] but not

Figure 1. Aleksandr Abramovich Grinberg, autographed portrait, date unknown [15]. (Photo courtesy of *Platinum Metals Review*.)

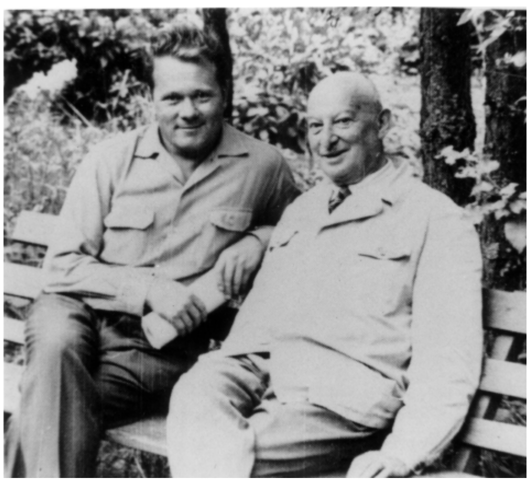


Figure 2. Grinberg and his former student Yurii Nikolaevich Kukushkin, author of one of the only two previous articles on Grinberg in English, 1964 [1]. (Photo courtesy of *Platinum Metals Review*.)

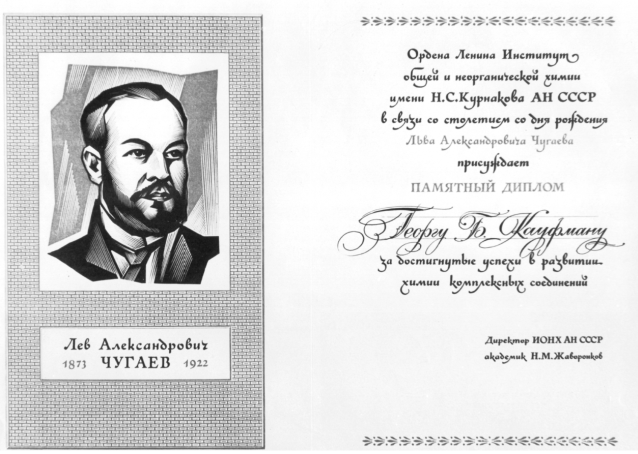


Figure 3. Lev Aleksandrovich CHugaev (1873–1922) (memorial diploma presented to George B. Kauffman on award of the Chugaev Bronze Medal, 1976). (Photo courtesy of George B. Kauffman.)

definitively proven until 1935 by Mills and Quibell's classic resolution [14].

Early Life [1, 2, 15–19]

Aleksandr Abramovich Grinberg was born on April 20 (Old Style—Julian—calendar; May 2 according to the New Style—Gregorian—calendar adopted by the Russian Soviet Federated Socialist Republic (RSFSR) on February 1, 1918—The USSR was not formed until December, 1922), 1898 in St. Petersburg, the capital of the Russian Empire. He was the son of Abram L'vovich Grinberg, a mining engineer, and Ekaterina Mikhailovna Grinberg (née Mysh), daughter of Mikhail Ignat'evich Mysh, a well-known St. Petersburg lawyer, who originated from the underclass of the Jewish Pale of settlement (those provinces of Czarist Russia where Jews were permitted to reside permanently according to a 1791 decree of Catherine II; permission to live outside its confines was granted only to certain groups such as members of the liberal professions, big businessmen, skilled artisans, etc.; the Pale was essentially abolished in August, 1915 and legally in March, 1917).

Young Aleksandr Abramovich was strongly influenced by his maternal grandfather, who talked at length with his grandchildren about history, literature, law, morality, and the humanities. He learned to read at an early age and had a passion for adventure stories such as the novels of James Fenimore Cooper. His father inculcated in him an interest and respect for the exact sciences and engineering, while his mother, whose knowledge of foreign languages allowed her to work as a scientific translator, inspired in him a love for music.

Beginning in 1908, Grinberg attended Gurevich's high school (*gymnasium*) in St. Petersburg, where he studied under such excellent teachers as historian and later Academician Boris Dmitrievich Grekov and Boris Mikhailovich Eikhenbaum, a well-known authority on Russian literature, who helped foster his interest in the humanities and literature. Unfortunately, the teaching in physics and chemistry was not very good. Grinberg always received the highest grades, and in 1916 he graduated with a gold medal.

On graduating, despite his interest in the humanities, Grinberg surprised everyone by becoming a student in the Medical Group of the Physico-Mathematical Faculty of Petrograd University. His decision may have been influenced by several of his friends who entered the same group. In 1917 the group moved to the First Petrograd Medical Institute (St. Petersburg was renamed Petrograd in 1914 because of anti-German sentiment occasioned by World War I; it was named Leningrad in 1924, and in 1991 the city reverted to its original name). It was here that Grinberg's interest in chemistry was aroused. At that time the university faculty included such luminaries of chemistry as Aleksei Evgrafovich Favorskii (1860–1945), Lev Aleksandrovich Chugaev (1873–1922) (Figure 3) [7b], Vladimir Nikolaevich Ipat'ev (1867–1952) [20], Mikhail Stepanovich Vrevskii (1871–1929), Viacheslav Evgen'evich Tishchenko (1861–1941), Yulii Sigizmundovich Zalkind (1875–1948), and Sergei Vasil'evich Lebedev (1874–1934) [21].

Under the influence of these men, especially the brilliant lectures and personal charisma of Chugaev, in 1918 Grinberg transferred to the newly organized Chemistry Department of the university's Physico-Mathematical Faculty. From this time on chemistry was his primary interest. In his own words, "I became a specialist in coordination chemistry thanks to

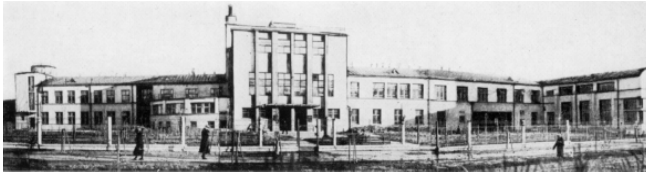


Figure 4. N. S. Kurnakov Institute of General and Inorganic Chemistry at Moscow from which the Izvestiia of the Platinum Institute was published for many years [23]. (Photo courtesy of *Platinum Metals Review*.)

РОССИЙСКАЯ АКАДЕМИЯ НАУК
КОМИССИЯ ПО ИЗУЧЕНИЮ ЕСТЕСТВЕННЫХ ПРОИЗВОДИТЕЛЬНЫХ СИЛ РОССИИ.

ИЗВЕСТИЯ ИНСТИТУТА
ПО ИЗУЧЕНИЮ ПЛАТИНЫ
и других благородных металлов.

под редакцией
Л. А. Чугаева
при содействии Н. К. Пшеницына и И. И. Черняева.

Том I.
Выпуск I.

ПЕТРОГРАД
1920.

Figure 5. Front cover of the first issue of the Izvestiia of the Platinum Institute published in Petrograd in 1920 [23]. (Photo courtesy of *Platinum Metals Review*.)

Chugaev" [2]. His friends later joked that "the chemists had stolen Aleksandr Abramovich from medicine" [1]. Grinberg, however, also retained his concern with medicine and biochemistry, and to the end of his life he retained these interests of his youth and later founded the Laboratory for the Study of Catalytic and Biological Properties of Complex Compounds at the N. S. Kurnakov Institute of General and Inorganic Chemistry (IONKh), situated at the Lensovet Technological Institute in Leningrad.

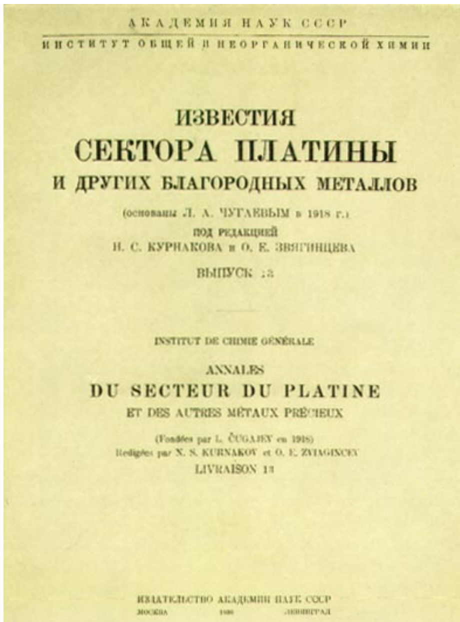
From 1919 to 1920 Grinberg was a junior scientific worker in the Russian Nutrition Institute. In 1919, while still a student, he presented the results of his first scientific research, supervised by Boris Ivanovich Slovtsov (1874–1924)—on the chemiluminescence of pyrogallol during its oxidation with hydrogen peroxide in the presence of potassium permanganate—to the Chemical Section of the Russian Physicochemical Society, resulting in his first publication [22]. In 1920 he became a junior scientific worker at the Natural Scientific Station of Petrograd State University.

The Platinum Institute

In 1915 Nikolai Semenovich Kurnakov (1860–1941) [7a], Vladimir Ivanovich Vernadskii (1863–1945) [7e], and Aleksandr Evgen'evich Fersman (1883–1945) had organized, as part of the Academy of Sciences, a Commission for the Study of Russian Natural Resources (KEPS). In response to the commission's request, Chugaev drafted a report in which he argued that platinum, one of Russia's most valuable natural resources, should not be exported in a raw form, but that a state monopoly be created for locating, producing, and processing this important metal. He proposed the formation of an institute with the following functions: comprehensive research on the metals of the platinum group (the last two triads of Periodic Group VIII—ruthenium, rhodium, palladium, osmium, iridium, and platinum); search for new and useful alloys of these metals; systematic study of the coordination compounds of these metals, including a search for new types of such compounds, their syntheses, reactions, and methods for determining their configurations; development and perfection of methods for the refining of the platinum metals as well as for the exploitation of low-grade ores.

It was only after the October Revolution of 1917 that Chugaev's dream became a reality. In 1918 the government of the newly formed RSFSR established a number of scientific research institutes, of which the Institute for the Study of Platinum and Other Noble Metals (Institut po Izucheniiu Platiny i Drugikh Blagorodnykh Metallov) of the Academy of Sciences of the USSR at Petrograd (founded in April, 1918) was one of the first (Figure 4). In accordance with the Soviet policy of creating a Russian chemical literature, in 1920, the year that Grinberg began to work at the institute, Chugaev founded the *Izvestiia Instituta po Izucheniiu Platiny i Drugikh Blagorodnykh Metallov* (Figure 5) [23]. From 1921 to 1935 almost the entire Russian literature on platinum, including much of Grinberg's work, appeared in the twelve volumes of this journal. Beginning in 1936, the journal was renamed *Izvestiia Sektora Platiny I Drugikh Blagorodnykh Metallov* (Figure 6). It ceased publication in 1955, being displaced by the new *Zhurnal neorganicheskoi khimii* (*Russian Journal of Inorganic Chemistry*).

It was at the Platinum Institute, directed by Chugaev, an adherent of Alfred Werner's [24] coordination theory and the founder of Soviet coordination chemistry, that Grinberg began research in 1920 as a scientific worker and subsequently a chief scientific specialist until 1937. Although during his short career Chugaev created around himself a ranking school of organic chemists, it was the "Chugaev School" of inorganic chemists, which included, in addition to Grinberg, Ilya Il'ich Chernyaev (1893–1966) [7c], Vitalii Grigor'evich Khlopin (1890–1950), Viacheslav Vasil'evich Lebedinskii (1888–1956) [7d], Nikolai Konstantinovich Pshenitsyn (1891–1961), and Ernest Khristianovich Fritsman (1879–1942), that has achieved the greater fame. In 1934 the Platinum Institute, the Institute for Physicochemical Analysis, and the General Chemistry Laboratory of the USSR Academy of Sciences merged into the Institute of General and Inorganic Chemistry (IONKh, now the N. S. Kurnakov Institute) with headquarters in Moscow [25].


АКАДЕМИЯ НАУК СССР
ИНСТИТУТ ОБЩЕЙ И НЕОРГАНИЧЕСКОЙ ХИМИИ

ИЗВЕСТИЯ
СЕКТОРА ПЛАТИНЫ
И ДРУГИХ БЛАГОРОДНЫХ МЕТАЛЛОВ
(основаны Л. А. ЧУГАЕВЫМ в 1918 г.)
под редакцией
Н. С. КУРНАКОВА и О. Е. ЗВЯГИНЦЕВА
ВЫПУСК 13

INSTITUT DE CHIMIE GÉNÉRALE
ANNALES
DU SECTEUR DU PLATINE
ET DES AUTRES MÉTAUX PRÉCIEUX
(Fondées par L. ČUGAJEV en 1918)
Rédigées par N. S. KURNAKOV et O. E. ZVIAGINCEV
LIVRAISON 13

ИЗДАТЕЛЬСТВО АКАДЕМИИ НАУК СССР
МОСКВА ЛЕНИНГРАД

Figure 6. In 1936 the title of the Izvestiia was amended to show its connection with the Institute of General and Inorganic Chemistry [23]. (Photo courtesy of *Platinum Metals Review*.)

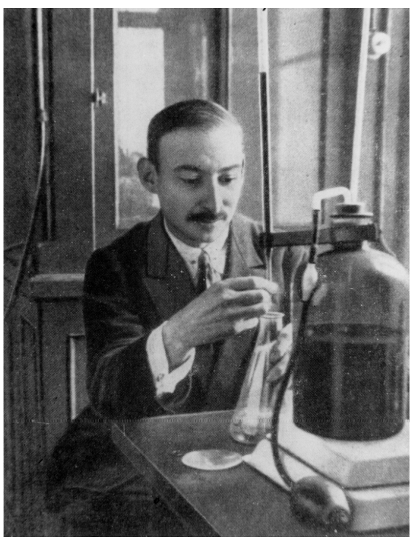


Figure 7. Grinberg in the Leningrad Laboratory of The Institute of General and Inorganic Chemistry, 1931 [18]. (Photo courtesy of Professors Yurii S. Varshavskii and Mark I. Gel'fman.)

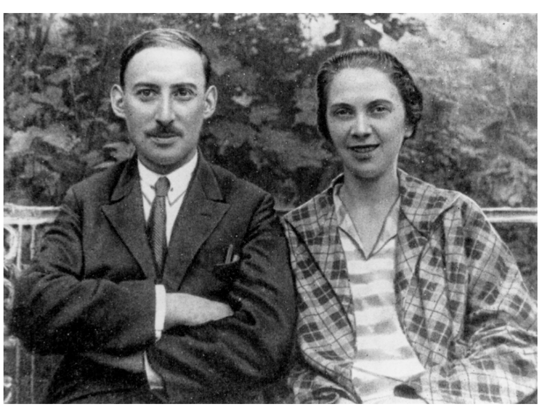


Figure 8. Grinberg and his wife, 1929 [18]. (Photo courtesy of Professor Yurii S. Varshavskii.)

Academic Career

In 1924 Grinberg graduated from the Leningrad State University, and his article "Beitrag zur Theorie der Indikatoren" [26], which in the following year won him the Small Aleksandr Mikhailovich Butlerov Award. (Two Butlerov awards were established in 1887 by the Russian Physicochemical Society; the small one was intended to encourage young chemists in their first independent work.) From 1928 to 1930 Grinberg was an assistant at the Second Medical Institute. In 1928 he became *Privat-Dotsent*; in 1931, *Dotsent* (Figure 7); and in 1932, Professor in the Chair of Inorganic and Analytical Chemistry at the I(van) P(etrovich) Pavlov Leningrad First Medical Institute where he remained until 1947.

In 1928 Grinberg married Varvara Borisovna Fratkina (Figure 8), a deeply intellectual, cultivated, and wise woman who became his faithful friend and advisor for the rest of his life. A kind and hospitable hostess, she entertained in their city house and their cottage in Komarovo near St. Petersburg, which were always open to Grinberg's colleagues and friends. In 1931 Grinberg participated in the work of the USSR Academy of Sciences' Soviet Platinum Expedition for the study of the productive power in the Ural Mountains and Altai (Figure 9). From 1932 to 1946 he was Professor at the Leningrad Extramural Industrial Institute.

During the period 1934–1949 Grinberg served as a consultant and group leader at the Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR (Leningrad). In 1935 he qualified as scholar for the People's Ministry of Common Health of the Russian Soviet Federated Socialist Republic (RSFSR) with the rank of Professor, and in that same year he was awarded the degree of Doctor of Chemical Sciences (*Doktor khimicheskikh nauk*) without the need for a dissertation.

In 1937 Grinberg became Professor of General and Inorganic Chemistry at the Leningrad (Lensovet) Institute of Technology, a chair that he retained until his death in 1966. Here he created a large and famous school of coordination chemists specializing in the chemistry of the platinum metals, who have carried on his work after his death.

During World War II (1941–1945) Grinberg and the Institute of Technology were evacuated from Leningrad to Kazan, about 450 miles east of Moscow, the town made famous in the annals of chemistry by the stereochemical work of Aleksandr Mikhailovich Butlerov (1828–1886) and the discovery of ruthenium by Karl Karlovich Klaus (1796–1864). Here Grinberg served as Professor of General Chemistry at the S(ergei) M(ironovich) Kirov Kazan Chemico-Technological Institute and the V(ladimir) I(l'ich) Ul'ianov-Lenin Kazan State University, where his collaboration with Aleksandr Ermingel'dovich Arbuzov (1877–1968), a prominent authority on the chemistry of organophosphorus compounds and discoverer of the Arbuzov reaction of alkyl phosphites, led to the founding of a laboratory for the study of coordination compounds of platinum with organic phosphorus ligands, which is still active today.

In 1943 Grinberg also became Laboratory Director of the V(italii) G(rigor'evich) Khlopin Radium Institute, which had been moved to Kazan from Leningrad, where the first European cyclotron was commissioned in 1936. During the pre-war years, when this institute was still in Leningrad, he

Figure 9. Grinberg (center) and Orest Evgen'evich Zviagintsev (right) on a steamship at the time of the Ural–Altai expedition, 1931 [18]. (Photo courtesy of Professor Yurii S. Varshavskii.)

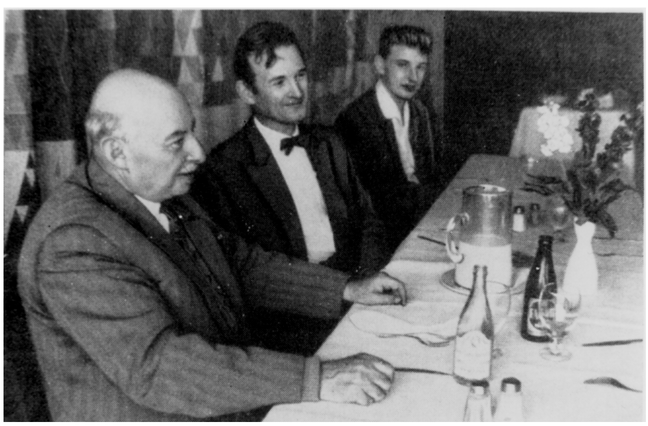


Figure 10. Grinberg (left) at the time of a trip to Sweden, with Lars Gunnar Sillén (center), 1961 [18]. (Photo courtesy of Professor Yurii S. Varshavskii.)

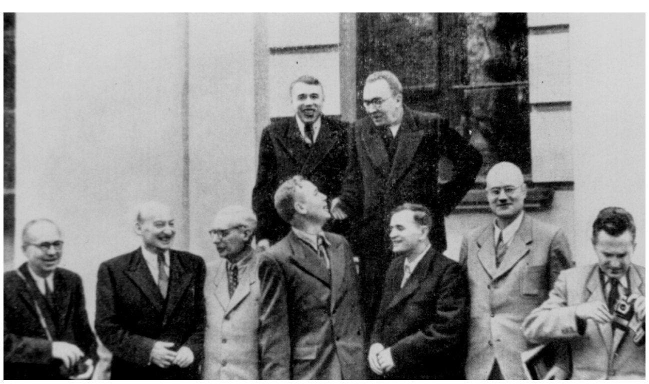


Figure 11. Grinberg (2nd from left) with other participants at the VIII All-Union Conference on the Chemistry of Complex Compounds, Kiev, 1960 [18]. (Photo courtesy of Professor Yurii S. Varshavskii.)

employed this cyclotron in collaboration with Filipp Mikhailovich Filinov [27] to obtain radioisotopes of platinum, iridium, and bromine, which he used in the study of coordination compounds. He retained this directorship until his death. He also served as Professor in the Chemistry Department of the A(ndrei) A(leksandrovich) Zhdanov Leningrad State University from 1947 to 1949.

Grinberg was an inspiring lecturer. The words that he spoke in praise of his mentor Chugaev could be applied equally to him: "Excellent scientist, splendid lecturer and speaker, who had a gift of putting forth his thoughts very clearly both orally and in writing, he personified an ideal man in science" [2]. As a teacher he was extremely tactful and considerate to his students and co-workers. In the words of co-worker Anna Dmitrievna Gel'man, "His well-meaning criticism forced us to take a fresh look at one's own work, to find some new aspects in it, and to advance what was already done. Grinberg restricted himself to clapping someone on the shoulder from the very top of his academic position, but was actively interested in the work and liked to carry on a discussion 'on equal terms'" [2].

Grinberg's standards for graduate students were extremely high. Receiving a "good" or "excellent" grade for the oral examination was quite difficult. Grinberg's usual grade was "accepted" (the lowest grade). When he recorded this grade, he always said, "*You* know chemistry for 'accepted;' *I* know for 'good,' and *only the Lord* knows for 'excellent'."

Because many new solutions to problems are often found at the boundaries between the various fields of science, Grinberg, a versatile scientist of wide and multifaceted interests, thought that too specialized an education is harmful for a researcher. He therefore favored the pre-1916 curriculum at the Natural Science Division of the Physico-Mathematical Department that required university students specializing in chemistry also to study anatomy, botany, geology, meteorology, and zoology. He also thought that scientists would beefit from a knowledge of Latin. As we have seen, early in his career Grinberg took an active interest in biochemistry and later was concerned with the catalytic and biological properties of coordination compounds.

Later Years

Grinberg was a member of the Commission for the Awarding of the L. A. Chugaev Prize (1949–1953) and was appointed a member of the editorial board of *Radiokhimiia* (1958) and the *Zhurnal neorganicheskoi khimii* (*Journal of Inorganic Chemistry*) (1959). In 1960 he became a member of the Board of the Leningrad Section of the Society for the Dissemination of Political and Scientific Knowledge and a member of the Scientific Consulting Council on the Computer and Informational-Logical Methods of Chemistry. A popular and much sought-after speaker, he lectured in various countries such as Czechoslovakia (1958, 1960), Poland (1959), and Sweden (Figure 10) and Denmark (1960, 1961), where he visited scientific institutes. Whenever possible, he participated in the International Conferences on Coordination Chemistry (ICCC) and other conferences on this subject (Figures 11–14).

As a lifetime authority on the coordination chemistry of platinum, at the time of his death Grinberg was working on a paper, "O Znachenii Platinovykh Kompleksov dlia Koordinatsionnoi Khimii" (On the Importance of Platinum Complexes for Coordination Chemistry), to be presented at the 9th International Conference on Coordination Chemistry, to be

Figure 12. Group of participants at the all-union conference on cobalt and nickel, left to right: Fiodor Yakovlovich Kul'ba, Mikhail Iosifovich Gil'Dengershel', Grinberg, Khodi Khakimovich Khakimov, Il'ia Il'ich Chernyaev, Anton Vasil'evich Ablov; Kishinev, 1960 [18]. (Photo courtesy of Professor Yurii S. Varshavskii.)

Figure 13. Grinberg in 1960 [18]. (Photo courtesy of Professor Yurii S. Varshavskii.)

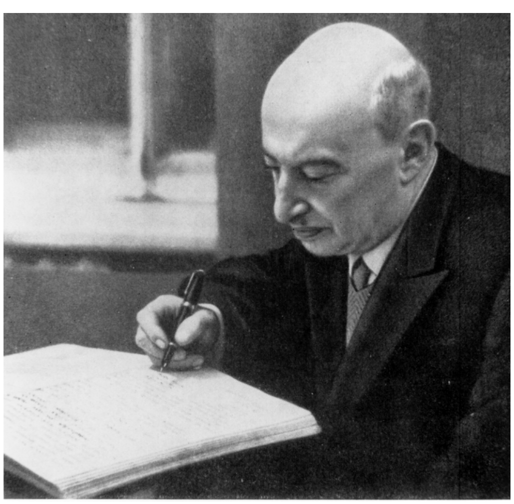


Figure 14. Grinberg writing in the honorary visitor book at the Dmitrii Ivanovich Mendeleev Museum on the day of the XV Mendeleev lecture, February 9, 1961 [18]. (Photo courtesy of Professor Yurii S. Varshavskii and Mark I. Gel'fman.)

held in St. Moritz, Switzerland on September 5–9, 1966 to celebrate the centenary of Werner's birth. Unfortunately, Grinberg died in Leningrad on July 1, 1966. Fortunately, this paper has been preserved for us in the literature [28].

Books

In 1936 the Russian edition of Alfred Werner's classic *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (*Newer Ideas in the Field of Inorganic Chemistry*), appeared in the USSR, where it was approved as a university textbook [29]. Grinberg wrote a 26-page essay, "O prirode sil kompleksoobrazovaniia" (On the Nature of the Force of Complex Formation) for the volume, of which his mother, Ekaterina Mikhailovna Grinberg, was cotranslator.

Grinberg's Stalin Prize-winning monograph *Vvedenie v khimiiu kompleksnykh soedinenii* (*Introduction to the Chemistry of Complex Compounds*) [30] appeared in three (1945, 1951, and 1956) editions and various translations (e.g., Polish and German, 1955; Chinese, 1956; Romanian, 1957; and Hungarian, 1958), and became a standard textbook widely used by undergraduate and graduate students as well as instructors and research workers in the USSR. Nevertheless, it was not until 1962 that chemists whose native language is English were able to consult this valuable monograph in a translation from the second Russian edition (1951) [31]. In a review of this translation, I stated:

> This readable translation of Grinberg's book will enable English-reading chemists to investigate for themselves the approach of the "Russian school" to coordination chemistry. This systematic survey, suitable as a text or reference book in intermediate or advanced inorganic chemistry courses, covers the entire field, largely from a physicochemical viewpoint, with emphasis on "descriptive" chemistry and stereochemistry. If the author seems to stress unduly the contributions of Russian chemists, it must be remembered that for many years the major proportion of research on platinum metal complexes, which are emphasized in this book, emanated from Russia and its world-famed Platinum Institute. The experimental and theoretical foundations of coordination chemistry, from its earliest beginnings up to 1951, are here discussed in a lucid and logical manner.... I unreservedly recommend it to instructors and students alike [32].

Honors and Awards

In 1941 Grinberg received the Lev Vladimirovich Pisarzhevskii Prize for his works on the physical chemistry of complex compounds. In 1943 he was elected a Corresponding Member and in 1958 an Academician of the USSR Academy of Sciences. In 1946 he was awarded the State (then Stalin) Prize, Second Class, for the first edition of his book *Vvedenie v khimiiu kompleksnykh soedinenii* (*Introduction to the Chemistry of Complex Compounds*) [30]. Among the other high government awards that he received for his scientific contributions and organizational activities was an Order of the Red Banner of Labor for outstanding service in the development of science and technology (on the occasion of the 220th anniversary of the Russian Academy of Sciences, 1945); Order of the Red Star for outstanding achievement in the field of radium therapy, the study of radioactive elements, and his work on the development of the nuclear industry in the Soviet Union (on the occasion of the 25th anniversary of the founding

Figure 15. Il'ia Il'ich Chernyaev (1893–1966), director of the Platinum Institute (1941–1966) [7D2]. (Photo courtesy of *Platinum Metals Review*.) Geometric Isomerism of Platinum(II) Complexes and Confirmation of their Square Planar Configuration.

of the Radium Institute, Academy of Sciences of the USSR, 1947); Order of Lenin (1953); and the title of Honorary Worker of Science and Technology of the Russian Soviet Federated Socialist Republic (RSFSR (1959).

When Grinberg first began his work on the coordination compounds of platinum, the square planar configuration of platinum(II) proposed by Werner on the basis of "isomer counting" and transformation reactions in his very first article on coordination chemistry [10a, pp 310–321; 10b, pp. 63–79], which we take for granted today, was not universally accepted. Because only a few platinum(II) and palladium(II) isomers were known and similar isomerism among complexes of other elements was not discovered for a number of years, this configuration was questioned more and more as time went by, and other grounds were adduced for the structure of these compounds [33]. For example, several workers [34] claimed to have isolated more than two isomers for compounds $[MA_2B_2]$, a fact that would eliminate a square planar configuration even though it is also incompatible with either the tetrahedral or square pyramidal arrangements. Furthermore, others claimed to have resolved tetrahedral platinum(II) complexes of type $[M(AB)_2]$, a fact inexplicable by the square planar configuration [35].

From molecular weight determinations in liquid ammonia Reihlen and Nestle [33a] concluded that *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ [11], the two prototypical isomers that played a crucial role in Werner's postulation of the square planar configuration, were not isomeric but that the latter was a dimer. Grinberg prepared the corresponding isomers of $[Pt(SCN)_2(NH_3)_2]$ and, on the basis of their molecular weights in acetone, which were equal, proved that they were indeed isomeric, thus supporting Werner's configuration [36].

In 1893 Kurnakov [37] had earlier used the reaction between thiourea and the *cis* and *trans* isomers of platinum(II) and palladium(II) to differentiate and identify these isomers [7b]. Grinberg added to "Kurnakov's reaction" the use of chelate ligands to perform this same task [38]. For example, he treated *cis*- and *trans*-$[PdX_2A_2]$ with oxalic acid or glycine and obtained in the case of the first isomer, $[Pt(C_2O_4)(NH_3)_2]$ or $[Pt(NH_2CH_2COO)(NH_3)_2]$ and obtained in the case of the second isomer *trans*-$[Pt(C_2O_4)_2(NH_3)_2]$ or *trans*-$[Pt(NH_2CH_2COOH)_2(NH_3)_2]$, that is, one molecule of the ligand reacts with one molecule of the *cis* isomer, but two molecules of the ligand react with one molecule of the *trans* isomer. Also, although previous attempts had been made to prepare the *cis* and *trans* isomers of $[Pt(NH_2CH_2COO)_2]$, Grinberg and Ptitsyn [39] succeeded in this synthesis, thus lending further support to Werner's postulated configuration. Grinberg and co-workers also determined dipole moments for various platinum(II) complexes to support the square planar configuration [40]. The unequivocal proofs for the square planar configuration were provided by Dickinson's crystal structure of $K_2[PtCl_4]$ [41] and Mills and Quibell's resolution of "*meso*-stilbinediamino*iso*butylenediaminoplatinous" salts [14].

Among the $[PdX_2A_2]$ isomers of palladium(II), where A is ammonia or an organic amine [42] the *cis* isomers are more difficult to isolate and are less stable than the corresponding platinum(II) compounds, and they readily isomerize to the *trans* isomers. Drew et al. [33c] and Grinberg [43] concluded that the compounds were not stereoisomeric but rather "polymerization isomers," $[PdX_2A_2]$ and $[PdA_4][PdX_4]$, and Drew rejected the existence of stereoisomerism among palladium(II) coordination compounds. The $[PdX_2A_2]$ compounds then known were believed to have the *trans* configuration so Grinberg applied the method for preparing *cis*-$[PtCl_2(NH_3)_2]$ to prepare the missing corresponding palladium(II) isomer, thus supporting the square planar configuration [44]. The unequivocal proofs for the square planar configuration were provided by Dickinson's crystal structure of $K_2[PdCl_4]$ and $(NH_4)_2[PdCl_4]$ [41] and Lidstone and Mills' resolution of "*meso*-stilbinediamino*iso*butylene-diamnopalladious" salts [45].

Mutual Influence of Ligands in the Coordination Sphere; Attempts to Explain the *Trans* and *Cis* Effects

Almost every student of organic chemistry knows that most substitution reactions do not occur in a random manner. For example, according to the Crum Brown–Gibson rule, certain groups on the benzene nucleus are *ortho*– or *para*–orienting, whereas others are *meta*–orienting. Similarly, substitution reactions among coordination compounds are not random, but the general rule governing the directed influences of coordinated ligands was not enunciated until well into the third decade of the 20th century. Such influences are most pronounced among square planar complexes, especially those of platinum(II) [31, Chapter 5].

The syntheses of these compounds, which were studied by Peyrone [46], Jørgensen [47], and Kurnakov [37], involved directive influences, but these were not generalized until Il'ia Il'ich Chernyaev's (Figure 15) classic account of the *trans* effect, one of Russia's greatest contributions to synthetic coordination chemistry [48]. This rule stated that a negative group coordinated to a metal atom loosens the bond of any group *trans* to it and thus explained not only Peyrone's, Jørgensen's, and Kurnakov's reactions but also many other features of the reactions of platinum(II) and (IV).

The first attempt to explain the effect was made by Chernyaev himself [48], who recognized that a simple coulombic treatment of the weakening or labilization of the *trans* bond was inadequate. Another early electrostatic theory was proposed in 1932 by Nekrasov [49]. Grinberg [50] noted that the *trans* effect for the series OH^-, Cl^-, Br^-, and I^- increased in an order corresponding to an increase in molar refraction, a fact which suggested that Kasimir Fajans' concept of polarizability [51] was pertinent here. Grinberg's polarization theory is the earliest theory of the *trans* effect that still has current application, and, together with Ryabchikov, he verified it with experimental data. He later developed a fruitful concept of the effect from the viewpoint of the reductive properties of ligands [52].

Throughout his career Grinberg carried out both theoretical and experimental studies of the *trans* effect. Together with Yurii Nikolaevich Kukushkin, he discovered a corresponding "*cis* effect" [53] during a study of the kinetics of reactions in which chloride atoms were substituted by ammonia in $[PtCl_4]^{2-}$ and $[PtCl_3(NH_3)]^-$. Because they found that the rate of substitution in the second ion is higher than in the first, they postulated that ligands in the *cis* position exert a "*cis* effect," which was confirmed by isotope exchange studies of chloride ligands. Later Grinberg initiated investigations to demonstrate this effect in analogous complexes with such ligands as pyridine, aliphatic amines, ethylene, thioethers, and sulfoxides in place of ammonia—studies that were finished by Kukushkin after Grinberg's death, and he showed that generally their *cis* effect was in the reverse sequence to their *trans* effect. Grinberg and Filinov also studied substitution reactions among platinum(IV) compounds. For example, they found that such reactions occur most readily with hexachloroplatinates(IV) in which two atoms of hlorine have been displaced by hydroxyl groups, i.e., $[Pt(OH)_2Cl_4]^{2-}$.

Kinetics of Ligand Substitution and Isotope Exchange Reactions; Thermodynamic and Kinetic Stability of Coordination Compounds in Solution

Although Grinberg is best known as an inorganic coordination chemist, he also made many contributions to fundamental and applied radiochemistry. He was one of the first to use radioisotopes in the study of the kinetics of coordination compounds, and he employed them to elucidate reaction mechanisms of complexes and the important role of solvents in reactions in solution.

For example, in 1939, by use of radioactive tracers, Grinberg and Filinov provided direct experimental proof of the lability and equivalence of all four of the bromide ions in $[PtBr_4]^{2-}$ and of all six of the bromide ions in $[PtBr_6]^{2-}$ [54]. This isotope exchange study showed that Werner's principal (*Hauptvalenzen*) and auxiliary (*Nebenvalenzen*) valences are indistinguishable and therefore identical. Grinberg also found that isotopic exchange of ligands in $[PtX_4]^{2-}$, where X is Cl^-, Br^-, I^-, or CN^-, paradoxically showed that the thermodynamic stability of the complexes did not agree with their kinetic lability but that the more stable the complex, the faster the ligands exchanged.

Grinberg's studies led to the extensive development of the kinetics of substitution and isotopic exchange and stimulated work on the determination of the consecutive and cumulative instability constants of platinum complexes and the investigation of the relationship between the kinetics and thermodynamics of coordination. In 1949 Grinberg and Nikol'skaiia [55] showed that for platinates(II) the more stable the complex, the more rapid is the exchange reaction. Grinberg later extended this result to substitution reactions in all platinum(II) complexes containing *trans*-active axes [30, 3rd ed., Chap. 10]. By the use of a platinized platinum electrode in platinum(II) salt solutions Grinberg and Gelf'man determined cumulative instability constants for platinum(II) complexes [56].

Grinberg's research on the kinetics of substitution reactions and isotope exchange of inner-sphere ligands allowed him to elucidate the mechanisms of numerous reactions and to show the important role of the solvent in such reactions. In aqueous solution many isotope exchange and basic hydrolysis reactions of platinum(II) complexes involve an initial aquation step, whereas in noncoordinating solvents they proceed by direct ligand substitution. For octahedral platinum(IV) complexes Grinberg found that the reaction mechanisms were more complicated and involved acid-base and redox properties. With his numerous studies from different viewpoints Grinberg demonstrated that coordination compounds are characterized by a greater variety of reactio mechanisms than are carbon compounds.

Acid-Base Properties of Coordination Compounds

Lev Aleksandrovich Chugaev [7b] had made valuable contributions to acid–base theory and the ability of coordination compounds such as acidopentaammines and acidoamidotetraammines of platinum(IV) to behave as acids: $M{-}RH \rightleftharpoons MR^- + H^+$ (where RH is a proton-containing ligand). Grinberg continued his teacher's work on the acid–base properties of coordination compounds by demonstrating the acidity of other coordinated proton-containing ligands as well as quantitatively measuring the acidities of amine and aqua complexes of various metals, resulting in useful generalizations permitting the prediction of properties of hitherto undiscovered compounds. His studies of the acidic properties of complex ammines and amines provided a basis for Basolo and Pearson's views on the mechanisms of substitution reactions, especially S_N1CB reactions.

Together with Gil'dengershel [57], Faerman [58], and other co-workers, Grinberg investigated the amido reaction and characterized both the amides and ammoniates of platinum(IV) by physicochemical methods [26, 59]. Grinberg's student Kukushkin [60] showed that in platinum(IV) complexes the *cis* effect is more important than the *trans* effect in determining the intensity of acidic properties, as Grinberg had shown previously for platinum(II), cobalt(III), and chromium(III) complexes. Grinberg and Kukushkin were able to combine studies of acid–base and redox properties and to show that if molecules of aliphatic diamines are coordinated to platinum(IV), the amido reaction:

$$Pt{-}NH_2R \rightleftharpoons Pt{-}NHR^- + H^+$$

is generally accompanied by reduction of platinum(IV) to platinum(II), apparently through platinum(III), and the formation in solution of free radicals capable of polymerizing acrylonitrile [61].

Oxidation-Reduction Reactions of Coordination Compounds

In 1933 Grinberg and Ptitsyn [62] showed that platinum(II) complexes could be oxidized quantitatively with potassium permanganate, a reaction that found application in analytical chemistry and led him to study systematically the redox properties of coordination compounds and to demonstrate the influence of ligands on redox potentials. On the basis of redox potential measurements Grinberg and co-workers developed a new physicochemical method for determining and confirming the structures of platinum compounds whose coordination formulas had been proposed by Werner by the use of synthetic methods and metatheses [63, 64]. For example, from the number of breaks in the potentiometric titration curves he was abl to differentiate the "monomeric" isomers *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ from the corresponding "polymeric" isomers, $[Pt(NH_3)_4][PtCl_4]$ (Magnus' green salt), $[PtCl(NH_3)_3][PtCl_3(NH_3)]$, $[PtCl(NH_3)_3]_2[PtCl_4]$, and $[Pt(NH_3)_4][PtCl_3(NH_3)]_2$ [64].

Grinberg carried out similar potentiometric titrations of systems containing oxidizable components such as the complex oxalates of platinum(II) and obtained similar results. Such systematic studies of the redox properties of coordination compounds of the platinum metals enabled Grinberg to devise a number of new methods for the volumetric determination of iridium and platinum in various combinations of oxidation states and in the presence of various admixtures [62, 65]. Grinberg and Filinov also studied in detail redox reactions (electron exchange) involved in the formation of "super complex compounds" (molecular compounds) from compounds of the same metal in different oxidation states such as those formed between $[PtBr_2(NH_3)_2]$ and $[PtBr_4(NH_3)_2]$ or between $[Pt(C_2H_5NH_2)_4]Cl_2$ and $[PtCl_2(C_2H_5NH_2)_4]Cl_2$ [66]. Their results were confirmed by subsequent X-ray diffraction studies [67].

Grinberg's Legacy

The breadth and scope of Grinberg's work and limitations of space have prevented me from discussing all of his multifaceted achievements, which, as the above treatment has shown, overlapped in various areas. For example, he played an active role in the Soviet nuclear program, working on uranium(IV) and uranium(VI) (UO_2^{2+}, uranyl) complexes, investigating redox reactions of uranium and transuranium elements with a number of oxidizing and reducing agents in various media, using complexation and chromatography for extraction, and developing an industrial method for the separation of plutonium from irradiated uranium. His radiochemical work has been discussed elsewhere [2].

Although among Werner's hundreds of students and one-time associates we encounter names of academic and industrial researchers, only a few of these men such as Paul Pfeiffer, Alexander Gutbier, or Yuji Shibata earned their reputations in the field of coordination chemistry. Thus there was no Werner school in the usual sense of the term, possibly because the impact of Werner's powerful and authoritarian personality and the impression of his control and mastery of his field may have deterred most of those who had worked with him from any thought of following in his footsteps. In other words, Werner's students respected and feared him rather than loved him. In contrast, Grinberg, with his genial personality and encouraging nature, became the leader of an influential, internationally renowned school of coordination chemists, who still continue today to carry out investigations whose roots can be found in his creative, pioneering studies.

Acknowledgment. I wish to acknowledge the assistance of Professors Yurii Sergeevich Varshavskii, Vadim Yur'evich Kukushkin, and Mark Iosifovich Gel'fman for critical readings of the manuscript and for providing valuable source materials. I am also indebted to Randy Vaughn-Dotta of the CSUF Academic Innovation Center for technical assistance.

References and Notes

1. Kukushkin, Y. N. *Platinum Metals Rev.* **1986**, *30*, 198.
2. Shashukov, E. A. *Radiochemistry* **1998**, *40*, 199; translated into English from *Radiokhimiya* **1998**, *40*, 193 (in Russian).
3. Kauffman, G. B. *Informatsionnyi listok (Uchebno-nauchnyi Tsentr Khimii Sankt-Peterburgskogo gosydarstvennogo universiteta* **Oct. 6, 1998**, No. *23/98* (76) (in Russian). Annually in early May Grinberg's former students, co-workers, and followers hold a meeting in his honor at the St. Petersburg State Technological Institute.
4. Kauffman, G. B. *Industrial Chemist* **Jan. 1987**, *8* (1), 40; *The World & I* **Jan. 1988**, *3* (1), 206; Kauffman, G. B.; Rae, I. D.; Solov'ev, Yu. I.; Steinberg, C. *Chem. Eng. News* **Feb. 16, 1987**, *65* (7), 28; Kauffman, G. B.; Solov'ev, Yu. I.; Steinberg, C. *Educ. Chem.* **1987**, *8*, 138; Bumpass, K.; Kauffman, G. B. *The Music Rev.* **Feb. 1988**, *48* (1), 43; Kauffman, G. B.; Bumpass, K. *Leonardo* **1988**, *21*, 429.
5. Figurovskii, N. A.; Solov'ev, Yu. I.; Steinberg, C.; Kauffman, G. B., Transl. *Aleksandr Porfir'evich Borodin: A Chemist's Biography*; Springer-Verlag: Berlin, Heidelberg, New York, 1988.
6. Kauffman, G. B.; Pinnell, R. P.; Takahashi, L. T. *Inorg. Chem.* **1962**, *1*, 544; Kauffman, G. B.; Tsai, J. H.; Jørgensen, C. K. *Inorg. Chem.* **1963**, *2*, 1233; Kauffman, G. B.; Benson, B. W. *Inorg. Chem.* **1967**, *6*, 411; Kauffman, G. B.; Anderson, G. L.; Teter, L. A. *J. Chromatog.* **1975**, *114*, 465; Kauffman, G. B.; Gump, B. H.; Stedjee, B. J. *J. Chromatog.* **1976**, *118*, 433; *J. Chromatog.* **1976**, *121*, 138; *J. Chromatog.* **1976**, *121*, 395; Kauffman, G. B.; Gump, B. H.; Stedjee, B. J.; Houghten, R. A. *J. Chromatog.* **1976**, *123*, 448.
7. (a) Kauffman, G. B.; Beck, A. *J. Chem. Educ.* **1962**, *39*, 44; *Polyhedron* **1983**, *2*, 855; (b) Kauffman, G. B. *J. Chem. Educ.* **1963**, *40*, 656; *Platinum Metals Rev.* **1973**, *17*, 144; (c) Kauffman, G. B. *Arch. Intern. d'Hist. Sci.* **1970**, *23*, 87; *Academic American Encyclopedia*; Aretê Publishing Co.: Princeton, NJ, 1980; Vol. 13, pp 294–295; (d) (1) Golovnya, V. A.; Leonova, T. N.; Craig, W.; Kauffman, G. B. *Ambix* **1976**, *23*, 187; (2) Kauffman, G. B. *Platinum Metals Rev.* **1976**, *20*, 126; (3) *J. Chem. Educ.* **1977**, *54*, 86; (e) *The World & I* **Aug 1980**, *5*(8), 318; Kauffman, G. B.; Miller, F. A. *J. Chem. Educ.* **1988**, *65*, 953; (f) Kauffman, G. B. *Platinum Metals Rev.* **1988**, *32*, 141; *Rhodium Express (St. Petersburg)* **1996**, *17*, 19; (g) Kauffman, G. B. *The World & I* **Oct. 1991**, *6* (10), 316; *S. African J. Sci.* **1996**, *92*, 519; *La Chimica nella Scuola* **1997** (May/June), *19* (3), 66; *Naturwiss. im Unterricht—Chemie* **Sept. 1997**, *8* (41), 46; *The Nucleus* **1998** (Sept.), *77*(1), 18.
8. Kauffman, G. B. Voprosy Istorii Estest. i Tekhn., Akad. Nauk SSSR **1969**, 4, 36, 118.
9. For example, Kauffman, G. B. *Inorg. Syn.* **1963**, *7*, 220, 228, 236, 249; **1967**, *9*, 182; Kauffman, G. B.; Cowan, D. O. *Inorg. Syn.* **1960**, *6*, 211, **1963**, *7*, 239; Kauffman, G. B.; Teter, L. A. *Inorg. Syn.* **1963**, *7*, 232, 245; *Inorg. Syn.* **1966**, *8*, 223; Kauffman, G. B.; Tsai, J. H. *Inorg. Syn.* **1966**, *8*, 217, 234; Kauffman, G. B.; Tsai, J. H.; Takahashi, L. T. *Inorg. Syn.* **1966**, *8*, 245; Kauffman, G. B.; Moravek, R. T. *Inorg. Syn.* **1986**, *24*, 217.
10. (a) Werner, A. *Z. anorg. Chem.* **1893**, *3*, 267; for an annotated English translation see (b) Kauffman, G. B. *Classics in*

Coordination Chemistry, Part 1: The Selected Papers of Alfred Werner; Dover Publications: New York, 1968, pp 9–88.

11. Kauffman, G. B.; Cowan, D. O. *Inorg. Syn.* **1963**, *7*, 239.
12. Kauffman, G. B. Curr. Contents: Phys., Chem., & Earth Sci. **Feb. 8, 1988**, 28 (6), 20.
13. Grinberg, A. A. *Z. anorg. allg. Chem.* **1927**, *164*, 207.
14. (a) Mills, W. H.; Quibell, T. H. H. *J. Chem. Soc.* **1935**, 839; for an annotated reprint see (b) Kauffman, G. B. *Classics in Coordination Chemistry, Part 3: Twentieth-Century Papers (1904–1935)*; Dover Publications: New York, 1978; pp 206–224.
15. Volshtein, L. M.; Finashin, G. N. *Aleksandr Abramovich Grinberg*; Izdatel'stvo Akademii Nauk SSSR: Moscow, 1963 (56 pp, with chronology and list of publications through 1962) (in Russian).
16. Kukushkin, Yu. N. *Zhurn. Neorg. Khim.* **1966**, *12*, 835 (in Russian).
17. Shchelokov, R. N., Ed. Vydayushchiesya Sovetskie Khimiki Akademiki A. A. Grinberg i I. I. Chernyaev; Nauka: Moscow, 1970 (71 pp) (in Russian).
18. Varshavskii, Yu. S.; Gel'fman, M. I. *Aleksandr Abramovich Grinberg 1898–1966*; Nauka: Leningrad, 1974 (119 pp) (in Russian).
19. Kukushkin, Y. N. Vestnik Rossiiskoi Akad. Nauk **1998**, 68, 422.
20. I am indebted to Louis Schmerling, Universal Oil Products Company, for the information that Chugaev was Ipat'ev's illegitimate maternal half-brother. See Eudin, X. J.; Fisher, H. D.; Fisher, H. H., Eds. *The Life of a Chemist: Memoirs of Vladimir N. Ipatieff*; Stanford University Press: Stanford, CA, 1946.
21. Solov'ev, Yu. I. Istoriia Khimii v Rossii: Nauchnye Tsentry i Osnovnye Napravleniia Issledovanii; Nauka: Moscow, 1985 (415 pp) (in Russian).
22. Grinberg, A. A. *Zhurn. Russ. Fiz.-Khim. Obshchestva, Chast' Khim.* **1920**, *52* (1), (4–6), 151 (in Russian).
23. Kauffman, G. B. *Platinum Metals Rev.* **1974**, *18*, 142.
24. Kauffman, G. B. *Alfred Werner: Founder of Coordination Chemistry*; Springer-Verlag: Berlin, Heidelberg, New York, 1966.
25. Solov'ev, Yu. I. *Institut Obshchei i Neorganicheskii Khimii im. N. S. Kurnakova Rossiiskoi Akademi Nauk: Istoricheskoi ocherk*; Nauka Publishing House: Moscow, 1993 (in Russian); for a review of this book see Kauffman, G. B. *Ambix* **1994**, *41*, 59.
26. Grinberg, A. A. *Z. anorg. allg. Chem.* **1924**, *138*, 333 (in German).
27. Grinberg, A. A. *Zhurn. Neorg. Khim.* **1958**, *3*, 2593 (obituary) (in Russian).
28. Grinberg, A. A. *Zhurn. Neorg. Khim.* **1967**, *12*, 842 (in Russian); *Russ. J. Inorg. Chem.* **1967**, *12*, 444 (in English).
29. Werner, A. *Novye vozzreniia v oblasti neorganicheskoi khimii;* 5th ed.; Matisen, S. A.; Grinberg, E. M., Transl.; Grinberg, A. A.; Ptitsyn, B. V., Eds.; Khimteoret: Leningrad, 1936 (in Russian).
30. Grinberg, A. A. *Vvedenie v Khimiiu Kompleksnykh Soedinenii* ; Goskhimizdat: Moscow, Leningrad, 1945 (366 pp); 2nd ed.; Goskhimizdat: Moscow, Leningrad, 1951 (464 pp); 3rd ed.; Izdatel'stvo "Khimiia": Moscow, Leningrad, 1966 (631 pp) (in Russian).
31. Grinberg, A. A. *An Introduction to the Chemistry of Complex Compounds*; Leach, J. R., Transl.; Busch, D. H.; Trimble, Jr., R. F., Eds.; Pergamon Press: Oxford, London, Paris, 1962.
32. Kauffman, G. B. *Science* **1963**, *139*, 480.
33. (a) Reihlen, H.; Nestle, K. T. *Ann.* **1926**, *447*, 211; (b) Angell, F. G.; Drew, H. D. K.; Wardlaw, W. *J. Chem. Soc.* **1930**, 349; (c) Drew, H. D. K.; Pinkard, F. W.; Preston, G. H.; Wardlaw, W. *J. Chem. Soc.* **1932**, 1895.
34. Drew, H. D. K.; Pinkard, F. W.; Wardlaw, W.; Cox, E. G. *J. Chem. Soc.* **1932**, 988, 1004.
35. Reihlen, H.; Hühn, W. *Ann.* **1931**, *489*, 42; **1932**, *499*, 144; Rosenheim, A.; Gerb, L. *Z. anorg. allg. Chem.* **1933**, *210*, 289; Reihlen, H.; Seipel, G.; Weinbrenner, E. *Ann.* **1935**, *520*, 256.
36. Grinberg, A. A. *Izv. Inst. Platiny* **1928**, *6*, 122 (in Russian).
37. Kurnakov, N. S. *J. Russ. Phys. Chem. Soc.* **1893**, *25*, 565 (in Russian); *J. prakt. Chem.* **1894**, [2] *50*, 481 (in German).
38. Grinberg, A. A. *Izv. Inst. Platiny* **1931**, *8*, 93 (in Russian).
39. Grinberg, A. A.; Ptitsyn, B. V. *Izv. Inst. Platiny* **1932**, *9*, 55 (in Russian).
40. Grinberg, A. A.; Razumova, Z. A.; Troitskaiia, A. D. *Izv. Akad. Nauk* SSSR, *Otd. Khim. Nauk* **1946** (No.3), 253; Grinberg, A. A.; Troitskaiia, A. D. *Izv. Lenin Tekhnol. Inst*. **1950**, *17*, 15 (in Russian).
41. Dickinson, R. G. *J. Am. Chem. Soc.* **1922**, *44*, 2404; reprinted with annotations in reference 14b, pp 116–126.
42. Krauss, F.; Brodkord, F. *Z. anorg. allg. Chem.* **1927**, *165*, 73.
43. Grinberg, A. A. *Izv. Inst. Platiny* **1933**, *11*, 95 (in Russian).
44. Grinberg, A. A.; Shul'man, V. M. *Dokl. Akad. Nauk* **1933**, *5*, 215; Grinberg, A. A.; Shul'man, V. M.; Khorunzhenkov, S. I. *Izv. Inst. Platiny* **1935**, *12*, 131 (in Russian).
45. Lidstone, A. G.; Mills, W. H. *J. Chem. Soc.* **1939**, 1754.
46. Peyrone, M. *Ann.* **1844**, *51*, 1.
47. Jørgensen, S. M. *J. prakt. Chem*. **1886**, [2] *33*, 489; *Z. anorg. Chem*. **1900**, *24*, 153.
48. Chernyaev, I. I. *Izv. Inst. Platiny* **1927**, *5*, 118 (in Russian); for an annotated English translation see reference 14b, pp 151–195.
49. Nekrasov, B. V. *Kurs Obshchei Khimii*; Moscow, Leningrad, 1935, Vol. 2; p 777; *Zhur. Obshchei Khim.* **1937**, *7*, 1594 (in Russian).
50. Grinberg, A. A. *Izv. Inst. Platiny* 1**932**, *10*, 47 (in Russian).
51. Fajans, K. *Z. Electrochem*. **1928**, *34*, 502; *Struct. Bonding* **1967**, *2*, 88.
52. Grinberg, A. A. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1943** (No. 5), 350 (in Russian).
53. Grinberg, A. A.; Kukushkin, Yu. N. *Zhur. Neorg. Khim*. **1957**, *1*, 106 (in Russian).
54. Grinberg, A. A.; Filinov, F. M. *Dokl. Akad. Nauk SSSR* **1939**, *23*, 918 (in Russian).
55. Grinberg, A. A.; Nikol'skaiia, L. E. *Zhur. Prikl. Khim*. **1949**, *22*, 542 (in Russian).
56. Grinberg, A. A.; Gel'fman, M. I. *Dokl. Akad. Nauk SSSR* **1960**, *133*(5), 1081; **1961**, *137*, 87.
57. Grinberg, A. A.; Gil'dengershel', Kh. I. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1948** (No. 5), 479.
58. Grinberg, A. A.; Faerman, G. P. *Zhur. Fiz. Khim*. **1931**, *2*, 161.
59. Grinberg, A. A. *Izv. Inst. Platiny* **1931**, *8*, 93; *Zhur. Fiz. Khim*. **1933**, *4*, 201.
60. Kukushkin, Yu. N. *Zhur. Neorg. Khim*. **1957**, *2*, 2371; **1962**, *7*, 769.
61. Grinberg, A. A.; Kukushkin, Yu. N. *Dokl. Akad. Nauk SSSR* **1961**, *140*, 1076.
62. Grinberg, A. A.; Ptitsyn, B. V. *Izv. Inst. Platiny* **1933**, *11*, 77.
63. Grinberg, A. A.; Riabchikov, D. I. *Dokl. Akad. Nauk* **1937**, *14*, 119; *Zhur. Fiz. Khim*. **1938**, *12*, 59.
64. Grinberg, A. A.; Kats, N. N. *Izv. Akad. Nauk SSSR, Otd. Mat. Estest. Nauk* **1938**, 941; **1943,** 8.
65. Grinberg, A. A.; Ptitsyn, B. V. *Izv. Inst. Platiny* **1935**, *12*, 133; *Dokl. Akad. Nauk* **1933** (No. 6), 284; **1936**, *3* (1), 17; Grinberg, A. A.; Mikhelis, Yu. L. *Dokl. Akad. Nauk* **1936**, *2*(5), 178; Grinberg, A. A.; Maksumiuk, E. A. *Izv. Sektora Platiny* **1946**, *20*, 149; Grinberg, A. A.; Maksumiuk, E. A.; Ptitsyn, B. V. *Dokl. Akad. Nauk* **1946**, *51*(9), 687.
66. Grinberg, A. A.; Filinov, F. M. Izv. Akad. Nauk SSSR, Otd. Mat. Estest. Nauk, Ser. Khim. **1937**, 908; Izv. Akad. Nauk SSSR, Otd. Khim. Nauk **1941** (No. 3), 361.
67. Brosset, C. *Arkhiv Kemi, Min., Geol*. **1948**, *25* (19), 1.