A Russian Pioneer in Platinum Metals Research

THE LIFE AND WORK OF LEV ALEKSANDROVICH CHUGAEV

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This year marks the 100th anniversary of the birth of Lev Aleksandrovich Chugaev (1873–1922), the foremost figure and undisputed leader of a group of Russian chemists who systematically explored the coordination compounds of platinum and its congeners. Chugaev's versatility rivalled that of Mendeleev, his predecessor in the chair of inorganic chemistry at the University of St. Petersburg. His scientific contributions ranged through bacteriology, biochemistry, organic chemistry (especially that of the terpenes), optical rotatory dispersion, coordination compounds, and analytical chemistry. He was also founder and first director of Russia's world-famed Platinum Institute.

Chugaev is best known for his discovery in 1905 of the scarlet precipitate formed by the reaction of the nickel(II) ion with dimethylglyoxime, the first organic spot test reagent used to detect a metal ion. Yet this prolific worker, for whom chemistry was paramount and for whom personal life was almost nonexistent, produced more than a hundred other articles during his short scientific career. The purpose of this paper is to review briefly Chugaev's life and research on the platinum metals.

Chugaev's Life

Lev Aleksandrovich Chugaev was born on October 4th, 1873, in Moscow and received his primary education in a military academy (1, 2, 3). As a student at Moscow University, he studied inorganic chemistry under I. A. Kablukov and organic chemistry under N. D. Zelinskii, with whom he published his first chemical paper in 1895. Following his graduation in that year, he was appointed assistant in the Chemical Laboratory of the Bacteriological Institute. In 1903, he successfully defended his dissertation "Issledovanie v Oblasti Terpenov i Kamfary" (Research in the Area of Terpenes in Camphor) and was granted the degree of

Lev Aleksandrovich Chugaev
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The first director of the Russian Platinum Institute and a prominent worker in coordination chemistry, Chugaev is credited with influencing practically the entire Russian output of researches on the chemistry of the platinum metals

Master of Chemistry. From 1904 to 1908, he was Professor at the Moscow Technical Institute. In 1906, he was awarded the degree of Doctor of Chemical Sciences for the successful defence of his dissertation "Issledovanie v Oblasti Kompleksnykh Soedinenii" (Research in the Area of Complex Compounds). In 1908, he was appointed Professor of Inorganic Chemistry at the University of St. Petersburg. He occupied this chair, which was formerly held by Mendeleev, Konovalev, and Walden, until his death at the age of 49. Later he simultaneously occupied the chair of organic chemistry at the Leningrad Chemico-Technological Institute.

Chugaev's premature death can be attributed directly to the deplorable conditions in post-revolutionary Russia. When life in Petrograd had become almost impossible, he moved his wife and two sons to Vologda, a city some hundred miles north of Moscow. During one of his visits to his family he contracted typhus, to which he succumbed on September 26th, 1922. His death was a serious loss for chemistry in general and a real disaster for Russian chemistry in particular.

Chugaev's earliest works were primarily biochemical and bacteriological. He investigated phosphorescent bacteria, triboluminescence, and the relationship between the structure of poisons and their toxicity. In organic chemistry, Chugaev concentrated on the terpenes; his most outstanding contribution to this field was the xanthogen method, which made possible the conversion of alcohols into their corresponding optically pure unsaturated terpene hydrocarbons. Chugaev's versatile reaction clarified an extremely complex area of organic chemistry and is still widely used in organic synthesis. With the pure, optically active compounds placed at his disposal by his xanthogen method, Chugaev turned to studies of the optical properties, particularly anomalous rotatory dispersion, of organic compounds, an area in which he became a world authority.

Although he was trained as an organic chemist, it is in coordination chemistry, a field in which he worked from 1904 until his death, that Chugaev's fame securely rests. Aside from his discovery of the nickel-dimethylglyoxime reaction, most of Chugaev's work on coordination compounds involved the stability of chelate rings. As early as 1906, Chugaev demonstrated that Baeyer's strain theory was applicable to coordination compounds and that 5- and 6-membered rings are more stable than 4- and 3-membered rings (4). The widely used diagnostic method for determining the configuration of platinum(II) coordination compounds by reaction with oxalic acid, subsequently developed by Chugaev's student A. A. Grinberg, provides an excellent example of the stability of a 5-membered ring (5).

Platinum Compounds

To quote Raleigh Gilchrist, "the character of practically the entire Russian output of researches on the chemistry of the platinum metals reflects the influence of Chugaev" (6). Since for many years Russian chemists have made more contributions to this field than those of any other nation, this is no mean achievement. Chugaev, like chemists before him and after him, realised that stereochemical studies of coordination compounds could best be made with elements whose complexes were stable and reacted with retention of configuration, i.e. with the platinum metals.

Chugaev's earliest and most extensive research in this field dealt with coordination compounds of organic sulphides and disulphides (7). Werner's coordination theory predicts only two stereoisomers (*cis* and *trans*) for compounds of type $[MA_2B_2]$ if the configuration is square planar. In an important study (8) Chugaev showed by its reaction with $[Pt(NH_3)_4]Cl_2$ to give insoluble Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, that the third (γ) isomer of $[Pt\{(CH_3)_2S\}_2Cl_2]$ was actually an electrolytic "polymerisation" isomer, $[Pt\{(CH_3)_2S\}_4][PtCl_4]$, rather than a stereoisomer. Under certain conditions, such as heating, the "polymerisation" isomer may decompose to form the monomer (9).

In accordance with Chugaev's rule of rings, organic disulphides were found to form more stable complexes than do the monosulphides (10). By conductance measurements Chugaev was able to follow the course of reactions and determine the relative stabilities of different ring systems. Use of the same physicochemical method (11) to determine the extents of dissociation and reaction of the isomers of organic monosulphides such as $[Pt(Et_2S)_2Cl_2]$ (12) led Chugaev to conclusions which were later explained by his student I. I. Chernyaev in terms of the "trans effect" (13).

Another series of platinum complexes to which Chugaev devoted much time were the chloropentaammines of platinum(IV). Every book on coordination chemistry includes almost without exception the familiar V-shaped plot of the molar conductances of the series of Pt(IV) ammines versus the number of chlorine atoms introduced into the coordination sphere. This graphical presentation usually omits the fact that the crucial second series in this group of Pt(IV) ammines, the chloropentaammines which were predicted by Werner's theory, were missing until Chugaev was finally able to synthesise them in 1915 (14). In view of its importance in the development of coordination chemistry, in 1925 $[Pt(NH_3)_5Cl]Cl_3$ was officially named "Chugaev's salt" by decree of the Fourth Mendeleev Congress.

The newly discovered Pt(IV) acidopentaammines also enabled Chugaev to make a valuable contribution to acid-base theory. The classical studies in this area by Niels Bjerrum and J. N. Brønsted had shown that hydrates, especially those of highly charged metallic ions, are acidic since the coordinated water molecules can lose protons to form hydroxoaquo complexes. Chugaev showed that an analogous reaction takes place with ammines but to a lesser extent than with hydrates, and he simultaneously discovered a new series of acidoamidotetraammines of Pt(IV) (14, 15). He also prepared a new series of Pt(IV) hydroxopentaammines and showed that $[Pt(NH_3)_5OH]^{3+}$ is a much weaker base than the corresponding cobalt(III) complex, $[Co(NH_3)_5OH]^{2+}$, which has a smaller charge (14–16).

Chugaev made a thorough study of the nitro complexes of divalent platinum and of the relationships between the reactions of the members of the series $[Pt(NH_3)_4](NO_2)_2$, $[Pt(NH_3)_3NO_2]NO_2$, *cis*- and *trans*-$[Pt(NH_3)_2(NO_2)_2]$, and $K_2[Pt(NO_2)_4]$ (17). He first prepared and established the structures of coordination compounds of platinum-containing ligands such as aminoacetal (18), nitriles (19), isonitriles (20), hydroxylamine (16, 21), water (22), the sulphito group (23), and hydrazine (24). Chugaev was also interested in the conversion of Pt(II) complexes to Pt(IV) complexes; he employed hydrogen peroxide (25), ozone (25), oxygen (26), and peroxydisulphate ion (26) as oxidising agents.

In addition to preparing new platinum complexes, Chugaev devised improved methods for the synthesis of known compounds, e.g. the valuable intermediate "Cleve's triammine", $[Pt(NH_3)_3Cl]Cl$, which he (27) synthesised from one of the best known Pt(II) complexes, Peyrone's salt, *cis*-$[Pt(NH_3)_2Cl_2]$ (28). He also devised a valuable test to distinguish *cis*-$[Pt(NH_3)_2Cl_2]$ from its *trans* isomer (29). A novel method utilising platinum black for the quantitative reduction of K_2PtCl_6 to K_2PtCl_4 constituted a great improvement over existing procedures (30).

Compounds of Other Platinum Metals

By use of thiourea, Chugaev prepared a new brilliant red osmium(III) compound, $[Os(NH_2CSNH_2)_6]Cl_3.H_2O$, the formation of which provided a sensitive analytical test by means of which one part of osmium can be detected in 100,000 parts of water (31). Evidence for the acidic nature of osmium

(VIII) oxide was shown by Chugaev's preparation of a series of well-defined crystalline compounds, $M_2[OsO_4(OH)_2]$, and unstable compounds, $M_2[OsO_4F_2]$ (32).

Chugaev's investigations of complexes of palladium with organic monosulphides and disulphides showed these compounds to be intermediate in properties between the corresponding complexes of nickel and platinum (33). His studies of hydrazine complexes of iridium led to the discovery of $H[Ir(N_2H_5)Cl_5]$ and its salts (34). He devised a novel method for detecting iridium in the presence of other platinum metals (sensitivity, 1 part of Ir in 6 million parts of water) (35). He also discovered a series of complex nonelectrolytes of the type $[Rh(NH_3)_3X_3]$ (36) and by use of rhodium black at 100° was able to convert catalytically a mixture of formaldehyde and sodium hydroxide to sodium formate (37).

Applied Works and the Platinum Institute

Chugaev was no "ivory tower" scientist. During World War I, in response to an increased demand for platinum catalyst to be used in the contact process for manufacturing sulphuric acid, Chugaev, together with Khlopin and Lebedinskii, devised industrial methods for the refining of platinum and its congeners. In 1915, N. S. Kurnakov, V. I. Vernadskii, and A. E. Fersman organised as part of the Academy of Sciences the Komissiya po Izucheniyu Estestvenno Proizvodstvennykh Sil Rossii, KEPS (Commission for the Study of Russian Natural Productive Sources). In response to this commission's appeal, Chugaev drafted a report arguing that platinum should not be exported in a raw form, but that a state monopoly be created for locating, producing, and processing this important natural resource. He proposed the formation of an institute for comprehensive research on the platinum metals with the following functions: search for new and useful alloys; systematic study (synthesis, reactions, and structure-proof) of old and new coordination compounds; development and perfection of methods for refining and analysis and for the exploitation of low-grade ores.

It was only after the October (1917) Revolution that Chugaev's dream became a reality. In 1918 he was appointed the first director of the newly created Institut po Izucheniyu Platiny i Drugikh Blagorodnykh Metallov (Institute for Study of Platinum and Other Noble Metals) of the Academy of Sciences of the USSR. On his death in 1922 Nikolai Semenovich Kurnakov (38) became director of the Institute.

In accordance with the Soviet policy of creating a Russian chemical literature, Chugaev founded the *Izvestiya Instituta po Izucheniyu Platiny i Drugikh Blagorodnykh Metallov* in 1920 to publish the Institute's research results. From 1921 to 1935, virtually the entire Russian literature on platinum metals appeared in the 12 volumes of this journal. In 1934, the Platinum Institute, the Institute of Physicochemical Analysis, and the General Chemistry Laboratory of the Academy of Sciences of the USSR merged into the Institut Obshchei i Neorganicheskoi Khimii, IONKh (Institute of General and Inorganic Chemistry), with headquarters in Moscow. Beginning with 1936 the journal was renamed *Izvestiya Sektora Platiny i Drugikh Blagorodnykh Metallov;* it ceased publication in 1955, being displaced by the new *Zhurnal Neorganicheskoi Khimii* (*Journal of Inorganic Chemistry*).

Unfortunately, Chugaev did not live to see the close cooperation which later developed between the Platinum Institute and Russia's platinum industry. Within a comparatively short time after his death, his ideas concerning the mutual dependence of theory and practice began to materialise, as the Institute rendered substantial aid to the young but growing industry. Even today Chugaev's former students continue to fulfil his prediction that "each and every scientifically founded conclusion or approximation, each pattern which conforms to a rule, each carefully established fact which is concerned with the chemistry of the platinum metals will sooner or later have its practical equivalent".

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