

Il'ya Il'ich Chernyaev's Research on the Platinum Metals

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This year marks the fiftieth anniversary of the trans effect, one of the most fundamental principles in the synthetic chemistry of the platinum metals, as well as the tenth anniversary of the death of its discoverer, Il'ya Il'ich Chernyaev, one of the Soviet Union's most distinguished scientists and the man who was undisputedly this century's most prolific worker on the coordination chemistry of platinum.

Il'ya Il'ich Chernyaev (1-9), late Academician of the Academy of Sciences of the U.S.S.R., was born on January 21, 1893 in the village of Spasskii in what was formerly Vologda province. After graduating from the Vologda Gymnasium (High School) with a gold medal in 1911, he entered the Natural Science Division of the Physico-Mathematical Faculty of St. Petersburg University where he studied under Lev Aleksandrovich Chugaev (1872-1922) (10). In 1915, he graduated with a first class diploma in chemistry, and at Chugaev's suggestion he remained at the university for training as a university teacher. He also began war research and work on platinum complexes in Chugaev's laboratory. His first published studies dealt with hydroxylamine (11) and aquo salts (12) of divalent platinum. In 1917, he became a contributor to the Platinum Division of the Commission for the Study of Russian Natural Productive Sources (KEPS) of the Russian Academy of Sciences. In 1918, he became Assistant in the Chair of Inorganic Chemistry at the Petrograd University and also became a research associate at Chugaev's newly created Institute for the Study of Platinum and Other Precious Metals at Petrograd. Until his death on September 30, 1966, he remained at this institute, which was transferred to Moscow in 1934 and underwent several changes in name through the years. Upon Chugaev's death in 1922, Nikolai Semenovich Kurnakov

(1860-1941) (13) became director of the institute, and on Kurnakov's death in 1941 it was renamed the N. S. Kurnakov Institute of General and Inorganic Chemistry of the Academy of Sciences of the U.S.S.R., with



Il'ya Il'ich Chernyaev
1893—1966

Academician of the Academy of Sciences of the U.S.S.R. and Professor of the Chemistry of Complex Compounds at the Lomonosov State University in Moscow, Chernyaev is remembered as one of the most prolific workers on the coordination chemistry of the platinum group metals

Chernyaev as its director, a post which he held until his death.

In 1923, Chernyaev became Assistant Lecturer at Petrograd University. In 1930, he became Docent in Inorganic Chemistry at the Leningrad Chemical-Technological University where he directed the Faculty of General Chemistry. In that same year he became Head Chemist of the Platinum Institute. In 1932, he was appointed Professor at Leningrad University, and in 1934, he took charge of the Section for the Chemistry of Complex Compounds in the newly created Institute of General and Inorganic Chemistry of the U.S.S.R. Academy of Sciences. From 1945 until his death he was Professor of the Chemistry of Complex Compounds at the Lomonosov State University in Moscow.

As Chugaev's successor and most outstanding student, Chernyaev was at the time of his death in charge of the world's largest school of chemists specialising in the chemistry of the platinum metals and one of the world's principal centres for the systematic study of coordination compounds in general. His name, of course, is inextricably linked with the *trans* effect and with numerous researches on the compounds of divalent and tetravalent platinum, especially those containing nitro groups. Less well known, however, is his role as one of the creators of refining technology in the Soviet precious metals industry. As such, his name is associated with a new and advanced method for the purification of platinum, its separation in highest purity, the preparation of pure osmium, a method for extracting platinum metals from low grade ores, the development of a series of analytical methods for noble metals, and the solution of many other critical industrial problems. Among the subjects included in his more than 275 articles are the synthesis, reactions, structure-proof, thermochemistry, thermodynamics, photochemistry, spectroscopy, and optical properties of complexes of the platinum metals. In the last decade of his life he helped to establish the nuclear fuel industry in the U.S.S.R. by his extensive

research on uranium and thorium complexes (7).

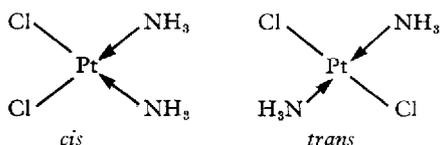
Chernyaev was the editor of many important monographs published by the Institute of General and Inorganic Chemistry. He was a co-editor of the Institute's journal, *Izvestiya Sektora Platiny i Drugikh Blagorodnykh Metallov* (14) from 1947 until 1955, when it ceased publication. In that year he became editor-in-chief of its newly founded successor, the *Zhurnal Neorganicheskoi Khimii*. For his discovery and application of the *trans* effect, Chernyaev received numerous awards and prizes from the Soviet government, including the Stalin Prize, First Class in Chemistry in 1952, four Orders of Lenin, and two Orders of the Red Banner of Labour. He was made a Corresponding Member of the U.S.S.R. Academy of Sciences in 1933 and an Academician in 1943.

Chernyaev's Work

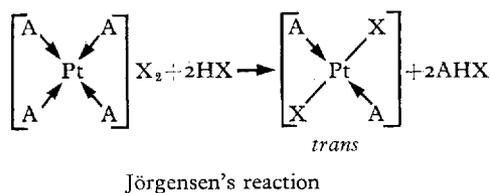
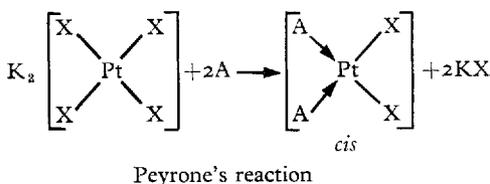
Almost every student of organic chemistry knows that most substitution reactions do not occur in a random manner, and in a similar manner, substitution reactions among coordination compounds are not random. However, the general principle underlying the directive influences of coordinated ligands was not enunciated until well into the third decade of the present century. Such influences are most pronounced and well investigated among square planar complexes, especially those of platinum(II).

The chemical behaviour of dipoisitive platinum complexes was studied by many of the early investigators in coordination chemistry, and the well-known regularities observed in substitution reactions were cited by Werner in his assignment of *cis* or *trans* configurations for platinum(II) complexes, to which he ascribed a square planar arrangement. The compounds chosen by Werner were among the simplest and longest known (1844) platinum isomers, viz., platosemi-diammine chloride or Peyrone's Salt and platosammine chloride or Reiset's Second Chloride, both with the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$.

On the basis of transformation reactions, Werner assigned them the configurations:

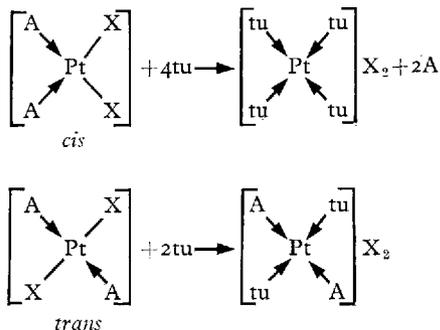


The synthesis of each of these compounds involves directive influences, and the preparative reactions were known as Peyrone's reaction and Jørgensen's reaction, respectively and were said to exemplify Peyrone's rule (*cis* orientation) (15) and Jørgensen's rule (*trans* orientation) (16):



(A = NH₃ or an amine, X = halogen)

In 1893, a third important regularity was observed by the Russian chemist Nikolai Semenovich Kurnakov (13), who found that substitution by thiourea occurs with all the ligands of the *cis* compound but only with the acid radicals of the *trans* compound (17):



(A = NH₃ or an amine, X = halogen or acid radical, tu = thiourea).

Since the two isomers yield different products, this reaction, known as Kurnakov's reaction or Kurnakov's test, may be used to differentiate *cis* from *trans* isomers of divalent platinum or palladium.

In 1926, Chernyaev (18, 19) generalised 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 divalent and tetravalent platinum. He also investigated substitution reactions of complexes of chromium, cobalt, tellurium, and osmium. He postulated that the *trans* effects of atoms are inversely proportional to their metallic character, i.e., directly proportional to their electronegativities. Electronegative ligands such as NO₂⁻, NCS⁻, F⁻, Cl⁻, Br⁻, and I⁻ have a greater "trans influence" than neutral ligands such as NH₃, amines, or H₂O. Chernyaev's original *trans*-directing series has been extended to include a variety of ligands: CN⁻ ~ CO ~ C₂H₄ ~ NO ~ H⁻ > CH₃⁻ ~ SC(NH₂)₂ ~ SR₂ ~ PR₃ > SO₃H⁻ > NO₂⁻ ~ I⁻ ~ SCN⁻ > Br⁻ > Cl⁻ > C₅H₅N > RNH₂ ~ NH₃ > OH⁻ > H₂O (20a).

Chernyaev's *trans* effect has been useful not only in synthetic work but also in structure-proof. His discovery enabled him and his many students and research workers to prepare many complexes not only of platinum but also of palladium, rhodium, iridium, ruthenium, cobalt, and other metals. The rule made it possible for the first time to plan systematic routes for carrying out inner-sphere substitution reactions in order to prepare platinum complexes in which all the ligands are different. For example, Chernyaev's early synthesis of the three possible geometric isomers of [Pt(NH₃)(C₅H₅N)(NH₂OH)(NO₂)]⁺ was cited as evidence for a square planar arrangement for platinum(II) (21). Among his syntheses of platinum(IV) complexes we may cite the following: [Pt₂(NH₃NO₂Cl₂)₂]⁺X⁻ (three out of four possible isomers and resolution of the two asymmetric compounds) (21, 22),

[Pt(NH₃NO₂BrCl)]X (five out of six possible isomers) (23), [Pt(NH₃)₂(NO₂)₂Cl₂] (all five possible isomers) (24).

Chernyaev's concept is one of the fundamental principles of synthetic inorganic chemistry and has greatly stimulated the theoretical study of the reactivity and kinetics of coordination compounds, and a number of reviews have been devoted to it (25, 26). At present there are two theoretical viewpoints concerning the possible mechanism of the *trans* effect.

The first type of theory is primarily an electrostatic one that emphasises a weakening or labilisation of the *trans* bond, suggested by Chernyaev himself (19), Nekrasov (27), and Grinberg (28). The second type of theory emphasises the lowering of the activation energy of *trans* replacement and makes use of modern molecular orbital theory (29-33). Two π -bonding ligands competing for the *d* orbitals of the metal tend to labilise each

other, compared to the more stable *cis* isomer where no competition takes place, and the stronger π -bonding will weaken the bonding of the ligand *trans* to it (20b). Several interpretations have also been made to explain the *trans* effect on the basis of σ -bonding only (34). It is currently uncertain what interpretation of the *trans* effect is the best.

Acknowledgements

The present study resulted from research on the separation of inorganic geometric isomers supported by the Research Corporation, the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society. The author, a Visiting Scholar at the Office for History of Science and Technology, University of California, Berkeley, acknowledges the John Simon Guggenheim Memorial Foundation for a Guggenheim Fellowship. He is also indebted to Drs G. V. Bykov, V. A. Golovnya, T. N. Leonova, and L. A. Nazarova, and the late Academician Il'ya Il'ich Chernyaev, all of the U.S.S.R. Academy of Sciences, for the location of source material, to Dr Henry M. Leicester and Alexander Beck for assistance in translation, and to Elsie Taylor and Robert Michelotti for technical assistance.

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The Electrodeposition of Osmium

Osmium is a rare metal with some unique properties. It has the highest work function of any metal and this has led to its use as thin coatings in thermionic devices. It has also been suggested that, because of its high melting point (3050°C), osmium could find application as a coating material for reed switches particularly at higher loads where arcing temperatures are greater. Such uses require the development of methods for producing thin coatings of the metal and a recent paper by J. N. Crosby, of International Nickel (*Trans. Inst. Metal Finishing*, 1976, **54**, (11), 75) describes a novel method for the electrodeposition of osmium.

The new electrolyte is prepared by reacting sulphamic acid with osmium nitrosyl complexes, in particular $K_2[Os(NO)(OH)(NO_2)_4]$. Bright osmium deposits are obtained in both acid and alkaline conditions. However, below pH 7 the current efficiencies are low (~2 per cent) and base metals such as copper have first to be given a protective gold coating. For maximum current efficiency (8 to 12 per cent) the preferred operating range is pH 12 to 14 when a deposition rate of 2 to 3 $\mu\text{m/hr}$ can be achieved. Plating performance is critically dependent on temperature and 70°C is the optimum. A plot of plating rate against current density shows the former to pass through a sharp maximum at 2 to 3 A/dm^2 . An advantage of this system is that it is not markedly dependent on osmium concentration so that it can be run for long periods without replenishment (e.g. from its normal level of 4 g/l Os down to 0.5 g/l Os).

However, this advantage is offset by the electrolyte's unfortunate characteristic of producing blackened deposits after a period of satisfactory operation.

Investigation of the blackening phenomenon showed that an anodic reaction plays a particularly important part in the bath's operation. If an electrolyte producing blackened deposits is operated in the cathode compartment of a divided cell the deposits soon improve and the normal mode of operation can then be resumed. However, continued use in the divided cell leads to a dramatic reduction in efficiency. Furthermore osmium cannot be deposited from a fresh electrolyte in such a cell. Thus a certain amount of anodic oxidation is necessary for the operation of the electrolyte but too much is deleterious. This is consistent with the fact that the current efficiencies of freshly prepared solutions tend to be very low initially and to rise during use.

The osmium deposits obtained under the preferred conditions are bright and adherent but are highly stressed and at thicknesses greater than 1 μm are microcracked. Deposits become dull and heavily cracked at thicknesses of ~6 μm .

An account is given of infra-red studies carried out to elucidate the nature of the electrolytes.

The need to operate this electrolyte with the intermittent use of a divided cell suggests that it is likely to find somewhat limited application, while the highly stressed nature of the deposits tends to reduce the useful thicknesses obtainable.

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