

Viacheslav Vasil'evich Lebedinskii

CENTENARY OF THE BIRTH OF A RHODIUM CHEMIST

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One of the lesser known members of the Chugaev school of inorganic chemists, Lebedinskii devoted more than four decades to the synthesis and analysis of co-ordination compounds of the platinum group metals, particularly those of rhodium, iridium, and platinum. He developed a new industrial method for purifying rhodium, and he carried out studies of the extraction and refining of the platinum metals and their separation from dilute solutions and salts.

Prerevolutionary Russia was the most important source of platinum, supplying about 95 per cent of the world's needs, and, despite the later discovery of extensive deposits of this noble metal elsewhere, the U.S.S.R. remains the leading producer of the platinum group metals — 3.7 million troy ounces compared to the 3.2 million ounces produced in the Republic of South Africa during 1985 (1). In

1828 the Russian government authorised the coinage of large amounts of Siberian platinum (2), and by 1846, when platinum coins were withdrawn from circulation, a total of 14,600 kilograms (39,117 troy pounds) of platinum had been coined in 3-, 6-, and 12-rouble denominations (3). Furthermore, ruthenium, the last of the platinum metals to be discovered, was isolated in 1844 by Karl Karlovich Klaus (1796–1864) from platinum residues obtained from Count Egor Frantsevich Kankrin (1775–1845) and named in honour of Russia (2b; 3, 4). Russia was also the home of the world-famous Platinum Institute of the U.S.S.R. and of the world's first platinum metals journal, *Izvestiia Sektora Platiny i Drugikh Blagorodnykh Metallov* (*Annals of the Sector for Platinum and Other Noble Metals*, hereafter called *Izvestiia* for the sake of



Viacheslav Vasil'evich Lebedinskii 1888–1956

Being one of the school of platinum metal chemists which formed around Chugaev, Lebedinskii was an acclaimed investigator and prolific writer on the platinum metals, with more than eighty papers on them to his credit. He also presented popular scientific lectures to soldiers, students and industrial workers. A Corresponding Member of the Academy of Sciences of the U.S.S.R. since 1946, by his work he contributed much to the knowledge of the platinum metals. He died on December 12th 1956 in Moscow

simplicity) (5). Thus it is not surprising that Russian chemists have been in the forefront of platinum metals research. Raleigh Gilchrist estimated that of the 800 articles on this subject published from 1915 to 1940, 28 per cent were contributed by Russians, with the Germans in second place, contributing 24 per cent (6).

Lev Aleksandrovich Chugaev (1873–1922) (7), founder and first director of the Platinum Institute and first editor of its *Izvestiia*, was the foremost figure and leader of a group of Russian chemists who systematically explored the chemistry and metallurgy of the platinum metals, and Gilchrist stated that “the character of practically the entire Russian output of researches on the chemistry of the platinum metals reflects the influence of Chugaev” (6). Chugaev created around himself a school of prominent platinum metal chemists, of whom Il’ya Il’ich Chernyaev (1893–1966), of *trans* effect fame, is the best known (8). Although another member of this group, Viacheslav Vasil’evich Lebedinskii, ranks second only to Chernyaev in the number of contributions published in the *Izvestiia* — 49 compared to 65 by Chernyaev — his name and work are little known in the West. The centenary of his birth seems an appropriate time to bring his work to the attention of a wider scientific audience.

Lebedinskii’s Academic Life

Viacheslav Vasil’evich Lebedinskii was born on 1st September 1888 in St. Petersburg (now Leningrad) (9). Upon his graduation from high school in 1907, he matriculated at the Petersburg University, graduating in 1913 with a First Degree Diploma. His thesis on the influence of optical superposition on anomalous rotatory dispersion was carried out under the direction of his teacher, Chugaev (10). He then remained at the university, working with Chugaev and preparing for a teaching career.

From 1916 Lebedinskii worked in the Platinum Section of the newly organised Commission for the Study of Russian Natural Productive Sources (KEPS). Beginning in 1918 he worked at the newly created Institute for the Study of Platinum and Other Noble Metals at

the Academy of Sciences of the U.S.S.R., in Leningrad, and he moved to Moscow in 1934 when the Platinum Institute merged with the Institute of Physicochemical Analysis and the General Chemistry Laboratory of the Academy of Sciences to become the Institute of General and Inorganic Chemistry, under the directorship of Nikolai Semenovich Kurnakov (1860–1941) (11). Lebedinskii became a member of the Scientific Council of the Institute and the Director of its Laboratory for the Synthesis of Complex Compounds.

From 1920 to 1935 Lebedinskii was Professor at Petrograd (later Leningrad) University, the Leningrad Chemico-Technological Institute, and the Second Leningrad Medical Institute. After he moved to Moscow in 1935 he was Professor at the M. V. Lomonosov Institute of Fine Chemical Technology and the Moscow Institute for Nonferrous Metals and Gold, both until 1952. He trained more than a score of Bachelors of Science candidates and several Doctors of Chemical Science.

Work on the Platinum Metals

Lebedinskii was the first to prepare stable cationic complexes of rhenium (11a, 12b), and he investigated compounds of cadmium halides with pyridine (13a) and aniline (13b). He also wrote articles on Stalin Prize winners (14a) and the life and work of Chugaev (14b) and of Chernyaev (14c). Except for an article on a palladium complex $[\text{PdCl}_2(\text{CH}_3\text{CN})_2]$ (15), the majority of his more than eighty papers on the platinum metals involved rhodium, iridium, and platinum, for the first two of which he achieved international recognition.

Rhodium

Dimethylglyoxime Complexes. Lebedinskii’s mentor, 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 (7, 16). Although a single oxime group shows little tendency toward co-ordination, when it can form part of a chelate ring, as in a dioxime, the

nitrogen atom becomes a good electron donor and hence a good ligand.

Lebedinskii's first postdoctoral research involved co-ordination compounds of rhodium(III) with dimethylglyoxime and is a continuation of Chugaev's classical work on dioximines (dioxime complexes). Together with Chugaev, he showed that hexa-covalent rhodium(III) formed two series of compounds with dimethylglyoxime ($\text{CH}_3\text{C}(\text{NOH})\text{C}(\text{NOH})\text{CH}_3$, DH_2), these being [a] $[\text{Rh}(\text{DH})_2(\text{NH}_3)_2]\text{X}$ (where $\text{X} = \text{Cl}, \text{I}, \text{OH}, \text{NO}_3, \text{ClO}_3, \text{ClO}_4, 1/2[\text{PtCl}_6]$, and $1/2[\text{PtBr}_6]$) and [b] $\text{R}[\text{RhCl}_2(\text{DH})_2]$ (where $\text{R} = \text{H}, \text{NH}_4$, or $(\text{NH}_2)_2\text{CNH}_2$ (guanidinium)) (17). The chloride of series [a] was prepared from $[\text{RhCl}(\text{NH}_3)_5]\text{Cl}_2$ and DH_2 , and the parent acid of series [b] from $\text{Na}_3[\text{RhCl}_6]$ and DH_2 . Each bidentate DH^- group is bonded to the rhodium atom by a co-ordinate covalent bond (through the oxygen atom) and a covalent bond (through the NOH group).

Twenty-five years later Lebedinskii and Fedorov obtained the compound $\text{NH}_4 \text{trans-}[\text{Rh}(\text{DH})_2(\text{NO}_2)_2] \cdot 2\text{H}_2\text{O}$ by boiling $\text{Na}_3[\text{RhCl}_6]$ solution with DH_2 and precipitating the resulting solution with NH_4Cl (18). By metathesis they obtained the corresponding guanidinium and tetra-ammineplatinum(II) salts. In 1948 they boiled solutions of $\text{NH}_4[\text{RhCl}_2(\text{DH})_2]$ with NH_4I , NH_4Br , NH_4SCN , and thiourea (tu) and obtained $\text{NH}_4[\text{RhCl}(\text{DH})_2] \cdot 1/2\text{H}_2\text{O}$, $\text{NH}_4[\text{RhBrCl}(\text{DH})_2] \cdot 2\text{H}_2\text{O}$, and also $\text{NH}_4[\text{RhClSCN}(\text{DH})_2]$, and the nonelectrolyte $[\text{RhCl}(\text{DH})_2(\text{tu})]$, respectively (19a). Boiling the ClI complex with thiourea results in substitution of the Cl atom but not the I atom, while similar treatment of the ClSCN complex causes substitution of the SCN group by thiourea. They also obtained (19b) the nonelectrolytes $[\text{Rh}(\text{DH})_2\text{NO}_2\text{NH}_3] \cdot 1/3\text{H}_2\text{O}$, $[\text{RhCl}(\text{DH})_2\text{NH}_3] \cdot \text{H}_2\text{O}$, and $[\text{Rh}(\text{DH})_2\text{Clpy}]$ (where $\text{py} = \text{C}_5\text{H}_5\text{N}$) by boiling DH_2 with $\text{K}[\text{Rh}(\text{NO}_2)_4(\text{NH}_3)_2]$ or $[\text{Rh}(\text{NO}_2)_3(\text{NH}_3)_3]$; $[\text{RhCl}_3(\text{NH}_3)_3]$; or $[\text{RhCl}_2\text{py}_4]\text{Cl}$, respectively.

Ammine. Lebedinskii applied Alfred Werner's co-ordination theory to rhodium(III)

and predicted that all the members of the transition series (*Übergangsreihe*) between the hexa-ammines and the double salts must exist, namely [i] $[\text{Rh}(\text{NH}_3)_6]\text{X}_3$, [iii] $[\text{RhX}(\text{NH}_3)_5]\text{X}_2$, [ii] $[\text{RhX}_2(\text{NH}_3)_4]\text{X}$, [iv] $[\text{RhX}_3(\text{NH}_3)_3]$, [v] $\text{M}[\text{RhX}_4(\text{NH}_3)_2]$, [vi] $\text{M}_2[\text{RhX}_5\text{NH}_3]$, and [vii] $\text{M}_3[\text{RhX}_6]$ (where $\text{X} =$ a uninegative anion and $\text{M} =$ a monopositive cation). Therefore he set about devising syntheses for compounds of the unknown series [iii], [iv], [v], and [vi]. In 1933 he obtained $(\text{NH}_4)_2[\text{RhCl}_4\text{NH}_3]$ (series [vi]) by boiling a $\text{Na}_3[\text{RhCl}_6]$ solution with NH_4Cl and $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, and he prepared the corresponding K^+ , Rb^+ , Cs^+ , and $[\text{Pt}(\text{NH}_3)_4]^{2+}$ salts by metathesis (20). In 1935, together with Fedorov, he prepared compounds of the corresponding acetonitrile series $\text{M}_2[\text{RhCl}_2\text{CH}_3\text{CN}]$ (where $\text{M} = \text{NH}_4$, K , Rb , Cs , Ag , or $1/2[\text{Pt}(\text{NH}_3)_4]^{2+}$) (21).

In the same year Lebedinskii prepared $[\text{RhCl}_3(\text{NH}_3)_3]$, a compound of the triammine series (series [iv]), by treating $\text{Na}_3[\text{RhCl}_6]$ with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ in the presence of $\text{HC}_2\text{H}_3\text{O}_2$ and NH_4Cl (22). In this work he showed how, by varying the ratios of the reactants, the corresponding mono-, tetra-, and pentaammines could be obtained. In this way he obtained for the first time $[\text{RhCl}_2(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O}$ (series [iii]). He concluded that rhodium(III) amines containing an odd number of ammonia molecules are much more stable and more easily synthesised than those containing an even number of ammonia molecules, probably because of the labilising action of anions in the *trans* position (Chernyaev's *trans* effect) (7, 23). He also found that this relationship was true for iridium(III) complexes.

Together with V. S. Volkov, Lebedinskii also prepared another triammine compound (series [iv]), namely $[\text{RhCl}_3(\text{tu})_3]$ as well as the additional thiourea complexes $[\text{Rh}(\text{tu})_6]\text{Cl}_3$ and $[\text{RhCl}(\text{tu})_5]\text{Cl}_2$ (24). In 1955, together with E. V. Shenderetskaya, he synthesised another triammine, $[\text{Rh}(\text{NO}_2)_3(\text{NH}_3)_3]$, by the reaction of ammonia with $\text{M}_3[\text{RhCl}_3(\text{NO}_2)_3]$. In this reaction all three chlorine atoms, which are *trans* to the nitro groups are labilised by them

since the nitro groups exert a strong *trans* effect. In this and numerous other reactions, Lebedinskii showed that Chernyaev's *trans* effect, first developed for platinum complexes, also applies to rhodium complexes. Lebedinskii also prepared the nitroammine complexes $[\text{RhNO}_2(\text{NH}_3)_3]\text{X}_2$ (series [ii]), $\text{M}[\text{Rh}(\text{NO}_2)_4(\text{NH}_3)_2]$ (series [v]), and $\text{M}_2[\text{Rh}(\text{NO}_2)_3(\text{NH}_3)]$ (series [vi]) (25). He also prepared the compounds $(\text{NH}_4)_2\text{Na}[\text{M}(\text{NO}_2)_6]$ (where M = Rh, Ir, or Co) (26).

Of the tetraammine series (series [iii]) only the $[\text{RhCl}_2\text{py}_4]\text{X}$ series was known (27) until, as mentioned above, Lebedinskii obtained compounds of the $[\text{RhCl}_2\text{py}_4]\text{X}$ series (22). He also synthesised the pyridine compounds $\text{M}[\text{Rh}(\text{NO}_2)_4\text{py}_2]$ (where M = Na, NH_4 , $(\text{NH}_2)_2\text{CNH}_2$, or $1/2[\text{Pt}(\text{NH}_3)_4]$) (28), $\text{M}[\text{RhCl}_4\text{NH}_3\text{py}]$ (where M = pyH , Ag, or $1/2[\text{Pt}(\text{NH}_3)_4]$), reference (29a), and $[\text{RhCl}_3\text{NH}_3\text{py}_2] \cdot 1/2\text{H}_2\text{O}$ (29b). In contrast to the ammonia complexes, he found that the most stable and most easily synthesised of the pyridine complexes are those with an even number of ammonia molecules, a relationship that he also discovered for iridium(III) complexes.

Lebedinskii and his co-workers also synthesised and characterised a large number of rhodium(III) complexes containing the sulphito group or the NaSO_3^- ion in the first coordination sphere, such as the complexes $\text{M}_2[\text{Rh}(\text{SO}_3)_2\text{NaSO}_3(\text{NH}_3)_3]$ (where M = Na, $1/2\text{Zn}$, $1/2\text{Ba}$, $1/2\text{Hg}$, or $1/2\text{Fe}$) (30), $\text{Ag}_3[\text{Rh}(\text{SO}_3)_3(\text{NH}_3)_3] \cdot 1/2\text{H}_2\text{O}$ (30), Na_3af , $\text{bc,de}[\text{Rh}(\text{SO}_3)_2\text{Na}(\text{SO}_3)_2(\text{NH}_3)_2]$ (31a), $\text{Na}_2[\text{Rh}(\text{SO}_3)_2\text{SO}_3\text{Na}(\text{NH}_3)_3] \cdot 6\text{H}_2\text{O}$ (31a), $\text{M}[\text{Rh}(\text{SO}_3)_2(\text{NH}_3)_4]$ (series [iii]) (where M = K, NH_4 , or Na) (31b). (In solution, the Na salt is in equilibrium with $[\text{RhSO}_3(\text{SO}_3\text{Na})(\text{NH}_3)_4]$, $\text{M}_3[\text{Rh}(\text{SO}_3)_3]$ (M = NH_4 or K) (31c), and $\text{M}[\text{Rh}(\text{SO}_3)_3(\text{NH}_3)_3]$ (where M = K or $(\text{NH}_2)_2\text{CNH}_2$) (31c). Lebedinskii also devised a procedure for separating rhodium from iridium with KI (32a) and developed a high-yield synthesis for $[\text{RhCl}(\text{NH}_3)_5]\text{Cl}_2$ (32b). His research on the sulphito complexes of

rhodium(III), specifically $(\text{NH}_4)_3[\text{Rh}(\text{SO}_3)_3]$ (31c), was used as the basis for the industrial preparation of spectroscopically pure rhodium metal, a method widely used in Russian refineries (33).

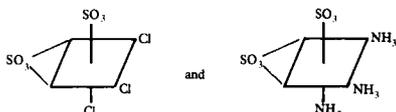
Iridium

Dimethylglyoxime Complexes. Lebedinskii and Fedorov synthesised dimethylglyoxime complexes of iridium(III) similar to those obtained with rhodium(III) and cobalt(III). These include $\text{M}[\text{IrCl}_2(\text{DH})_2](\text{M} = \text{H}, \text{NH}_4, \text{K}, (\text{NH}_2)_2\text{CNH}_2, \text{ or } 1/2[\text{Pt}(\text{NH}_3)_4])$ (34a), $\text{M}[\text{Ir}(\text{NO}_2)_2(\text{DH})_2](\text{M} = \text{H or } \text{NH}_4)$ (34b), $\text{H}[\text{IrNO}_2\text{X}(\text{DH})_2](\text{X} = \text{Cl or } \text{SCN})$ (34b), $[\text{Ir}(\text{DH})_2(\text{NH}_3)_2]\text{X}$ (X = I or picrate) (34c), and $[\text{Ir}(\text{DH})_2(\text{tu})_2]\text{I}$ (34c). They deduced the configurations of the compounds on the basis of Chernyaev's *trans* effect, which is valid for iridium compounds. For example, since the NH_3 molecule exhibits a higher degree of lability in the $[\text{Ir}(\text{DH})_2(\text{NH}_3)_2]^+$ ion as compared with that of the Cl atom in the $[\text{Ir}(\text{DH})_2\text{Cl}_2]^-$ ion, they concluded that the two NH_3 molecules are in *cis* positions relative to each other and in *trans* positions relative to the =NO groups of the DH^- groups (34c).

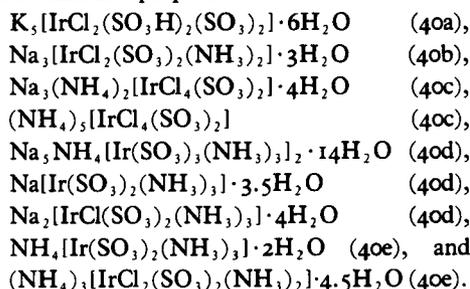
Amine and Ammine Complexes. In 1926 Lebedinskii prepared the first reported tris(ethylenediamine) complexes of iridium(III), namely $[\text{Ir}(\text{en})_3]\text{X}_3$ (where X = I, $1/2[\text{PtCl}_4]$, $1/2[\text{PtCl}_6]$, $1/2[\text{Pt}(\text{CN})_4]$, $1/2[\text{PtBr}_6]$, $1/2[\text{OsCl}_6]$, $1/4[\text{Fe}(\text{CN})_6]$, or $1/3[\text{Fe}(\text{CN})_6]$, and en = ethylenediamine) (35). In 1938 he and N. A. Balitskaya prepared the first compounds of the monoammine series, $\text{M}_2[\text{IrCl}(\text{NH}_3)]$ (where M = K, NH_4 , Rb, or $1/2[\text{Pt}(\text{NH}_3)_4]$) (36). The compounds are less susceptible to hydrolysis than the corresponding rhodium(III) compounds (series [vi]).

This monoammine series is analogous to the corresponding acetonitrile series $\text{M}_2[\text{IrCl}(\text{CH}_3\text{CN})]$ (where M = NH_4 , K, $(\text{NH}_2)_2\text{CNH}_2$, or $1/2[\text{Pt}(\text{NH}_3)_4]$) (37). With thiourea (tu) Lebedinskii obtained (24) the compounds $[\text{IrCl}_3(\text{tu})_3]$, $[\text{IrCl}_2(\text{tu})_4]\text{Cl}$, $[\text{IrCl}(\text{tu})_5]\text{Cl}_2$, and $[\text{Ir}(\text{tu})_6]\text{Cl}_3$ (38), analogous to the corresponding rhodium(III) compounds.

Sulphito Complexes. As in the case of rhodium(III), Lebedinskii and his colleagues made extensive studies of complexes of iridium(III) with the sulphito and NaSO_3^- groups as ligands, using Chernyaev's *trans* effect to elucidate the configurations (7, 23). With M. M. Gurin, he synthesised and characterised $\text{Na}_2[\text{Ir}(\text{SO}_3\text{Na})(\text{SO}_3)_2(\text{NH}_3)_3] \cdot 7\text{H}_2\text{O}$ (with NH_3 molecules *cis* to each other) (39a); $\text{Na}_3[\text{IrCl}_2(\text{SO}_3)_2] \cdot 7\text{H}_2\text{O}$ (39b), $\text{M}[\text{IrCl}_2(\text{SO}_3)_2] \cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{NaRb}$, or K) (39b), and $\text{Na}_7[\text{IrCl}_2(\text{SO}_3)_4]$ (39c). They also synthesised complexes in which the sulphito groups are mono- and bidentate in the same compound, for example, $\text{M}_4[\text{IrCl}_2(\text{SO}_3)_7]$, $\text{M} = \text{K}$ or NH_4 (if $\text{M} = \text{K}$ the compound is Claus' salt) (39d), and $\text{M}[\text{Ir}(\text{SO}_3)_2(\text{NH}_3)_3]$ ($\text{M} = \text{K}$ or $1/2\text{Zn}$) (39d). The configurations for the two anions are:



Working with Z. M. Novozhenyuk, Lebedinskii prepared and characterised:

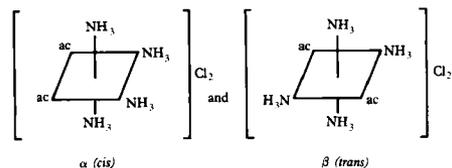


Platinum

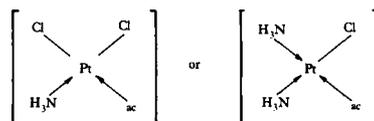
The chemistry of platinum has been more extensively investigated than that of any other of the platinum metals, and it played a prominent role in Werner's development of his coordination theory from its very inception (41). As is well known, divalent platinum has a coordination number of four and a square planar configuration, whereas tetravalent platinum has a coordination number of six and an octahedral configuration.

Acetonitrile Complexes. In opposition to this generalisation, Lebedinskii and his mentor

Chugaev reported the preparation of two platinum(II) complexes, which they claimed to be hexaco-ordinate, that is, to have a co-ordination number of six. They treated *cis*- and *trans*- $[\text{PtCl}_2(\text{ac})_2]$ (where $\text{ac} = \text{CH}_3\text{CN}$, acetonitrile) with ammonia and obtained water-soluble, colourless chlorides, α - and β - $[\text{Pt}(\text{ac})_2(\text{NH}_3)_4]\text{Cl}_2$, which contained chlorine atoms, both of which were ionised in solution and replaceable by $[\text{PtCl}_4]^{2-}$ and $(\text{C}_6\text{H}_3\text{O}_7\text{N}_3)^{2-}$ (picrate ions) (42a). Since the ammonia molecules were strongly combined in the new compounds, not being titratable with mineral acids, and since the ammonia could only be removed by boiling with hydrochloric acid, whereupon two molecules of ammonia and two molecules of acetonitrile were eliminated, the α -complex yielding *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ and the β -complex yielding *trans*- $[\text{PtCl}_2(\text{NH}_3)_2]$, Chugaev and Lebedinskii assigned to these complexes the structures:



Although these compounds have been cited in the literature, for instance (43, 44), as examples of hexaco-ordinate platinum(II), Lebedinskii and Golovnya later showed that these compounds, as well as the corresponding compounds that they had obtained with propionitrile, $\text{pn} = \text{C}_2\text{H}_5\text{CN}$, are better formulated as containing tetravalent platinum(II) in which two ammonia molecules are bonded to the nitrile molecules, for example, *cis*- or *trans*- $[\text{Pt}(\text{ac} \cdots \text{NH}_3)_2(\text{NH}_3)_2]\text{X}_2$ (45a,b). As evidence against a co-ordination number of six, they cited the facts that excess ammonia reacts with compounds such as:



(containing only one molecule of acetonitrile)

to yield neither a tetraammine nor a hexaammine but a pseudopentaammine, $[\text{Pt}(\text{ac})(\text{NH}_3)_4]\text{Cl}_2$ (which is actually $[\text{Pt}(\text{ac} \cdots \text{NH}_3)(\text{NH}_3)_3]\text{Cl}_2$) (45a,b). They also cited the action of boiling hydrochloric acid solution on both $[\text{Pt}(\text{ac})_2(\text{NH}_3)_4]\text{Cl}_2$ and $[\text{Pt}(\text{ac})(\text{NH}_3)_4]\text{Cl}_2$ in splitting off, for each molecule of acetonitrile, one molecule of ammonia, whereby *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ or $[\text{PtCl}(\text{NH}_3)_3]\text{Cl}$ is formed, respectively.

In addition, Chugaev and Lebedinskii prepared the compounds $M[\text{PtCl}_3(\text{ac})]$ (where $M = \text{K}$ or $1/2[\text{Pt}(\text{NH}_3)_4]$), showing that acetonitrile reacts with soluble tetrachloroplatinate(II) just as ammonia and organic amines do (45b). Lebedinskii and Golovnya also prepared numerous complexes of platinum with acetonitrile or propionitrile, including *cis*- $[\text{PtCl}_2(\text{pn})_2]$, *cis*- $[\text{PtCl}_2(\text{pn})\text{NH}_3]$, $[\text{PtCl}(\text{pn})(\text{NH}_3)_2]\text{X}$ ($\text{X} = \text{Cl}$ or I), $M[\text{PtCl}_3\text{pn}]$ ($M = \text{K}$ or $1/2[\text{Pt}(\text{NH}_3)_4]$), $[\text{Pt}(\text{ac})(\text{NH}_3)_3]\text{X}_2$ ($\text{X} = \text{Cl}$ or $1/2$ picrate), $[\text{Pt}(\text{pn})(\text{NH}_3)_4]\text{X}_2$ ($\text{X} = \text{Cl}$ or $1/2$ picrate), and $[\text{Pt}(\text{pn})_2(\text{NH}_3)_4]\text{Cl}_2$, and they found that propionitrile is less strongly bonded to platinum than is acetonitrile (45b). They also prepared "pseudohexaco-ordinate" complexes such as $[\text{PtX}_2\text{A}_2][\text{PtCl}_4]$ (where $\text{X} = \text{ac}$ or pn and $\text{A} = \text{methylamine}$, CH_3NH_2 , or ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$) (45d, e) and devised new syntheses for known compounds such as $\text{K}[\text{PtCl}_3\text{NH}_3]$ and $[\text{PtCl}_2(\text{NH}_3)_2]$ (45c).

Sulphito Complexes. In addition to their research on sulphito compounds of iridium, Lebedinskii and Novozhenyuk carried out similar studies with platinum, synthesising $\text{K}_4[\text{Pt}(\text{SO}_3)_2(\text{SO}_3\text{H})_2]$, $\text{M}_3[\text{PtCl}_2\text{SO}_3(\text{SO}_3\text{H})]$

(where $M = \text{K}$ or $1/2[\text{Pt}(\text{NH}_3)_4]$), and also $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{SO}_3)_2(\text{NH}_3)_2]$ (46a), $\text{K}_4[\text{Pt}(\text{SO}_3)_3\text{NH}_3]$, $\text{K}_2\text{cis}-[\text{Pt}(\text{SO}_3)_2\text{py}_2]$, and $[\text{PtSO}_3(\text{NH}_3)_2\text{py}]$ (46b). They demonstrated that the bond between the sulphito group and the central atom is stronger when the group occupies one co-ordination position instead of two (46a), and that the sulphito group exerts a strong *trans* effect (46c). Together with R. K. Korabel'nik, Lebedinskii synthesised new platinum complexes with aminosulphonic acid, namely, $\text{K}[\text{Pt}(\text{NH}_2\text{SO}_3)\text{Cl}_2\text{NH}_3]$ and $[\text{Pt}(\text{NH}_2\text{SO}_3)\text{Cl}(\text{NH}_3)_2]$ (47).

Extraction and Analysis of Ores. Lebedinskii and Khlopin developed a method for preparing pure platinum by boiling the ore with aqua regia and then precipitating the platinum as ammonium hexachloroplatinate(IV), $(\text{NH}_4)_2[\text{PtCl}_6]$, by the addition of ammonium chloride (48). As a member of the Analytical Commission of the Platinum Institute, Lebedinskii was involved in the development of several methods for analysing platinum ores (49, 50) as well as the extraction, separation and refining of the platinum metals. He also developed a spectroscopic method for detecting the presence of platinum in sulphur ores (51).

For some forty years Viacheslav Vasil'evich Lebedinskii was involved in research on the chemistry of the platinum metals. Although he is credited with the development of new industrial processes, much of his work was of a highly academic nature, so reinforcing the position of Russians at the forefront of platinum metals research. By his teaching he contributed to the continuation of this great tradition.

References

- 1 "Metal Statistics 1986", 79th Edn., Fairchild Publications, New York, 1986, p. 125
- 2 (a) Anon., *Philos. Mag.*, 1828, (2), 4, 458; (b) D. McDonald and L. B. Hunt, "A History of Platinum and its Allied Metals", Johnson Matthey, London, 1982, Ch. 13
- 3 B. N. Menshutkin, *Izv. Sektora Platiny i Drug. Blagorodn. Metal., Inst. Obshch. i Neorg. Khim., Akad. Nauk S.S.S.R.* (hereafter abbreviated *Izv.*), 1928, 6, 1-10; *J. Chem. Educ.*, 1934, 11, 226-229
- 4 M. E. Weeks, rev. by H. M. Leicester, "Discovery of the Elements", 7th Edn., Journal of Chemical Education, Easton, PA, 1968, pp. 418-425
- 5 G. B. Kauffman, *Platinum Metals Rev.*, 1974, 18, (4), 142-149; V. V. Lebedinskii, *Izv.*, 1924, 3, 81-84
- 6 R. Gilchrist, *Chem. Rev.*, 1943, 32, 277-372
- 7 G. B. Kauffman, *J. Chem. Educ.*, 1963, 40, 656-665; *Platinum Metals Rev.*, 1973, 17, (4), 144-148

- 8 G. B. Kauffman, *Platinum Metals Rev.*, 1976, **20**, (4), 126-130; *J. Chem. Educ.*, 1977, **54**, 86-89; V. A. Golovnya, T. N. Leonova, W. Craig and G. B. Kauffman, *Ambix*, 1976, **23**, 187-198
- 9 O. E. Zvyagintsev, *Zh. Neorg. Khim.*, 1957, **2**, 1713-1719
- 10 L. A. Chugaev and V. V. Lebedinskii, *Zh. Russ. Fiz. Khim. Obshch.*, 1913, **45**, 648
- 11 G. B. Kauffman and A. Beck, *J. Chem. Educ.*, 1962, **39**, 44-49; G. B. Kauffman, *Platinum Metals Rev.*, 1982, **26**, (3), 129-133; *Polyhedron*, 1983, **2**, 855-863
- 12 V. V. Lebedinskii and B. N. Ivanov-Emin, (a) *Zh. Obshch. Khim.*, 1943, **13**, 253-265; (b) *Zh. Neorg. Khim.*, 1959, **4**, 1762-1767
- 13 (a) V. V. Lebedinskii, I. S. Rassonskaya and S. N. Avakyan, *Dokl. Akad. Nauk S.S.S.R.*, 1954, **94**, 245-248; V. V. Lebedinskii and S. N. Avakyan, *Izv. Akad. Nauk Armyan. S.S.R., Khim. Nauki*, 1958, **11**, 321-325; (b) 1959, **12**, 91-93
- 14 V. V. Lebedinskii, (a) *Usp. Khim.*, 1943, **12**, 245-255; (b) *Izv.*, 1948, **21**, 18-26; (c) V. V. Lebedinskii and A. M. Rubenshtein, *Usp. Khim.*, 1953, **22**, 241-252
- 15 V. V. Lebedinskii, P. V. Simanovskii and O. D. Slutsker, *Izv.*, 1948, **21**, 43-53
- 16 L. A. Chugaev, *Z. anorg. Chem.*, 1905, **46**, 144-169; *Ber.*, 1905, **38**, 2520-2522
- 17 L. Tschugaeff and W. Lebedinskii, *Z. anorg. Chem.*, 1913, **83**, 1-7
- 18 V. V. Lebedinskii and I. A. Fedorov, *Izv.*, 1938, **15**, 19-25
- 19 V. V. Lebedinskii and I. A. Fedorov, *Izv.*, (a) 1948, **21**, 157-163; (b) 1948, **21**, 158-167
- 20 V. V. Lebedinskii, *Izv.*, 1933, **11**, 5-12
- 21 V. V. Lebedinskii and I. A. Fedorov, *Izv.*, 1935, **12**, 87-92
- 22 V. V. Lebedinskii, *Izv.*, 1935, **12**, 67-77
- 23 I. I. Chernyaev, *Izv.*, 1927, **5**, 118-156; for an annotated English transl. see G. B. Kauffman, "Classics in Coordination Chemistry, Part 3; Twentieth-Century Papers (1904-1935)", Dover Publications, New York, 1978, pp. 151-195
- 24 V. V. Lebedinskii and V. S. Volkov, *Izv.*, 1935, **12**, 79-86
- 25 V. V. Lebedinskii and E. V. Shenderetskaya, *Izv.*, (a) 1945, **18**, 19-22; (b) 1955, **31**, 53-55
- 26 V. V. Lebedinskii and E. V. Shenderetskaya, *Izv.*, 1955, **29**, 61-65
- 27 S. M. Jørgensen, *J. prakt. Chem.*, 1883, [2], **27**, 433-489
- 28 V. V. Lebedinskii and S. F. Silin, *Izv.*, 1937, **14**, 33-39
- 29 N. A. Vargunin, N. S. Kurnakova and V. V. Lebedinskii, *Sb. Nauch. Trudov. Krasnoyarsk. Med. Inst.*, (a) 1958, (5), 97-101; (b) *ibid.*, 101-102
- 30 V. V. Lebedinskii and N. N. Myasoedov, *Izv.*, 1939, **16**, 65-76
- 31 V. V. Lebedinskii and E. V. Shenderetskaya, *Izv.*, (a) 1948, **21**, 164-174; (b) 1955, **30**, 99-105; (c) *Zh. Neorg. Khim.*, 1957, **2**, 1768-1774
- 32 V. V. Lebedinskii, *Izv.*, (a) 1927, **5**, 364; (b) 1936, **13**, 9-17
- 33 V. V. Lebedinskii, E. V. Shenderetskaya and A. G. Maiorova, *Chist. Metal. i Poluprovod., Tr. 1-oi [Pervoi] Mezhd. Konf., Moscow, 1957, 235-238* (published in 1959); *Zh. Prikl. Khim.*, 1959, **32**, 928-929
- 34 V. V. Lebedinskii and I. A. Fedorov, *Izv.*, (a) 1938, **15**, 27-34; (b) 1945, **18**, 23-30; (c) *ibid.*, 31-37
- 35 V. V. Lebedinskii, *Izv.*, 1926, **4**, 235-242
- 36 V. V. Lebedinskii and N. A. Balitskaya, *Izv.*, 1938, **15**, 13-18
- 37 V. V. Lebedinskii and P. V. Simanovskii, *Izv.*, 1939, **16**, 53-56
- 38 V. V. Lebedinskii, E. S. Shapiro and N. P. Kasatkina, *Izv.*, 1935, **12**, 93-102
- 39 V. V. Lebedinskii and M. M. Gurin, *Compt. rend. acad. sci. U.R.S.S.*, (a) 1941, **33**, 241-243; (b) 1942, **36**, 22-25; (c) 1943, **38**, 128-130; (d) 1943, **40**, 322-325 (all in English)
- 40 V. V. Lebedinskii and Z. M. Novozhenyuk, *Izv.*, (a) 1955, **29**, 66-76; (b) 1956, **30**, 106-108; (c) *Zh. Neorg. Khim.*, 1957, **2**, 2490-2491; (d) 1958, **3**, 286-291; (e) 1958, **3**, 2462-2466
- 41 A. Werner, *Z. anorg. Chem.*, 1893, **3**, 267-330; for an annotated English translation see G. B. Kauffman, "Classics in Coordination Chemistry, Part 1: The Selected Papers of Alfred Werner", Dover Publications, New York, 1968, pp. 5-88
- 42 L. Chugaev and W. Lebedinski, *Compt. rend.*, (a) 1915, **161**, 563-564; (b) 1916, **162**, 43-45
- 43 A. Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie", rev. and ed. by P. Pfeiffer, Friedrich Vieweg, Braunschweig, 1923, p. 181
- 44 P. Pfeiffer, in "Stereochemie", ed. K. Freudenberg, Franz Deuticke, Leipzig, Vienna, 1933, p. 1252
- 45 V. V. Lebedinskii and V. A. Golovnya, *Izv.*, (a) 1939, **16**, 57-64; (b) 1945, **18**, 38-49; (c) 1947, **20**, 95-98; (d) 1948, **21**, 32-42; (e) 1948, **22**, 168-174
- 46 V. V. Lebedinskii and Z. M. Novozhenyuk, (a) *Izv.*, 1951, **26**, 83-94; (b) 1952, **27**, 80-88; (c) 1952, **27**, 89-98
- 47 V. V. Lebedinskii and R. K. Korabel'nik, *Izv.*, 1947, **20**, 99-106
- 48 V. V. Lebedinskii and V. G. Khlopin, *Izv.*, 1926, **4**, 317-323
- 49 S. F. Zhemchuzhnyi, O. E. Zvyagintsev, B. G. Karpov, V. V. Lebedinskii and N. I. Podkopaev, *Izv.*, 1926, **4**, 339; 1926, **4**, 340-343; 1926, **4**, 355-359
- 50 A. T. Grigoriev, S. F. Zhemchuzhnyi, O. E. Zvyagintsev, B. G. Karpov, N. S. Kurnakov, V. V. Lebedinskii and N. I. Podkopaev, *Izv.*, 1926, **4**, 343-355
- 51 O. E. Zvyagintsev, V. V. Lebedinskii and A. N. Filippov, *Compt. rend. acad. sci. U.R.S.S.*, 1933, 165-169