

Chernyaev2013: XX International Chernyaev Conference on Chemistry, Analysis and Technology of Platinum Group Metals

Highlights of the research and characterisation of platinum group metals and their compounds

<http://dx.doi.org/10.1595/147106714X679467>

<http://www.platinummetalsreview.com/>

Reviewed by Kirill V. Yusenko*

Department of Chemistry, Center for Materials Science and Nanotechnology, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

*Email: kirill.yusenko@smn.uio.no

Sergey I. Metelitsa** and Vladimir N. Losev‡

Scientific Research Engineering Centre «Kristall» of the Siberian Federal University, 79 Svobodny av., Krasnoyarsk, 660041 Russia

**Email: metelitsa_s1@mail.ru;

‡Email: losevvn@gmail.com

Introduction

The “XX International Chernyaev Conference on Chemistry, Analysis and Technology of Platinum Group Metals” was held at the Siberian Federal University in Krasnoyarsk, Russia, between 7th and 12th October 2013. This conference was dedicated to the 120th anniversary of Professor Ilya Il'ich Chernyaev (1893–1966) and the 70th anniversary of the Gulidov Krasnoyarsk Non-Ferrous Metals Plant; it was also a celebration of 70 years since the first International Chernyaev Conference on Chemistry, Analysis and Technology of Platinum Group Metals, which was held in 1943 in Sverdlovsk (now Yekaterinburg) under the chairmanship of Professor Chernyaev. All aspects of chemistry, analysis and especially refining of platinum group metals (pgms) are traditionally discussed during the conference. Strong industrial participation is an important part of the Chernyaev Conference series (1).

More than 200 participants attended Chernyaev2013 from Russia, Portugal, Norway, Finland, Latvia and Kazakhstan with 10 plenary lectures, 100 oral and 65 poster presentations divided into four sections:

- Chemistry of pgms and gold compounds;
- Analysis of pgms and Au;
- Production technology of pgms and Au;
- Application of pgms and Au in industry, catalysis and medicine.

The first school for young scientists followed after the conference and included four plenary lectures and thirteen oral presentations.

Chemistry of the Platinum Group Metals

Synthesis and investigation of various pgm coordination and organometallic compounds in

solid state and solution were the focus of the first session. Danila Vasilchenko (Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia) and co-authors reported the first detailed characterisation of $\text{H}_2[\text{Pt}(\text{OH})_6]$ in chloride-free nitric acid solutions in a broad range of concentrations (2). Several monomeric $[\text{Pt}(\text{L})_x(\text{NO}_3)_{6-x}]$ ($\text{L} = \text{H}_2\text{O}$ or OH^- ; $x = 0-6$) and dimeric $[\text{Pt}_2(\mu\text{-OH})_2(\text{NO}_3)_8]^{2-}$ anions were detected by ^{195}Pt nuclear magnetic resonance (NMR) in solution. Individual compounds such as $(\text{PyH})_2[\text{Pt}(\text{NO}_3)_6]$ and $((\text{CH}_3)_4\text{N})_2[\text{Pt}_2(\mu\text{-OH})_2(\text{NO}_3)_8]$ were also investigated structurally in solid state using Raman spectroscopy and single crystal X-ray diffraction (XRD). Solid $\text{H}_2[\text{Pt}(\text{OH})_6]$ and its nitric acid solution were proposed as starting species for the preparation of various Pt(IV) and Pt(II) coordination compounds and heterogeneous supported catalysts.

Ruslan Mullagaleev (Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia) and Sergey Korenev (Nikolaev Institute of Inorganic Chemistry) and co-authors showed the great potential of palladium solution in nitric acid (3, 4) and especially *trans*- $[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ (5) for synthesis of various monomeric and oligomeric Pd(II) species with promising industrial applications (6, 7). A halogen-free Pd(II) solution can easily be prepared by heating Pd powder in nitric acid, leading to formation of *trans*- $[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ in solution. Crystalline *trans*- $[\text{Pd}(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ can be prepared by slow evaporation of the solution and further utilised as a starting Pd(II) compound with high reactivity. **Figure 1** summarises possible reactions which can be used to synthesise coordination and organometallic compounds of Pd(II) with high yields.

Nitroso-ruthenium compounds have promising future applications in ruthenium coordination chemistry and refining from ores and secondary

sources as well as from nuclear wastes (8). Vyacheslav Emel'yanov (Nikolaev Institute of Inorganic Chemistry) showed a detailed overview of $[\text{RuNO}]$ -chemistry in aqueous chloride, nitride and ammonia solutions including a characterisation of species in solution and solid state as well as their transformations (9). NMR spectroscopy on ^{99}Ru , ^{14}N , ^{15}N and ^{17}O has been applied as the most informative tool for characterisation of various species in complex $\text{Ru-NO-Cl}^- \text{-NO}_2^- \text{-NH}_3 \text{-NO}_3^- \text{-H}_2\text{O}$ systems (**Table I**). The detailed analysis of NMR spectra may not only lead to an understanding of the chemical nature of target complexes but also propose reliable mechanisms for their formation and transformation. Powder X-ray diffraction (PXRD) and single crystal analysis have been applied for the characterisation of more than 50 Ru-based complexes in solid state over 30 years of intensive research at the Institute.

Analysis of Platinum Group Metals

Analysis of the pgms in various objects was discussed in the second section. Liudmila Zhitenko (the Russian State Precious Metals and Gems Repository, Gokhran) discussed fundamental and practical aspects of the analysis of pgms, Au and silver in cultural heritage samples. The most significant challenge for such samples is the practical impossibility of performing analysis in the laboratory; the analysis can be carried out only in their permanent places of storage, and must also be non-destructive. However, the analysis is not usually restricted by the need for high precision. Nowadays, portable, easy to use and precise equipment has been developed for use outside the laboratory such as in field-based analysis and museums. X-ray fluorescence spectroscopy (XFS), neutron activation analysis, laser spark emission spectrometry, inductively coupled plasma-mass spectrometry (ICP-MS) with

Table I

NMR data (δ , ppm) for Ruthenium Nitrosyl Chloro Complexes (Water, $\sim 20^\circ\text{C}$) (9)

Species	δ ^{99}Ru	δ ^{14}N	δ $^{17}\text{O}(\text{NO})$	δ $^{17}\text{O}(\text{H}_2\text{O})$
$[\text{RuNOCl}_5]^{2-}$	4190	-36	379	-
<i>trans</i> - $[\text{RuNO}(\text{H}_2\text{O})\text{Cl}_4]^-$	3920	-18	411	0 ± 10
<i>cis</i> - $[\text{RuNO}(\text{H}_2\text{O})\text{Cl}_4]^-$	4450	-	~ 380	$-71; -4^a$
<i>mer</i> - $[\text{RuNO}(\text{H}_2\text{O})_2\text{Cl}_3]$	4130	-18	413	-
<i>fac</i> - $[\text{RuNO}(\text{H}_2\text{O})_2\text{Cl}_3]$	4770	-	-	-

^a acetone solution

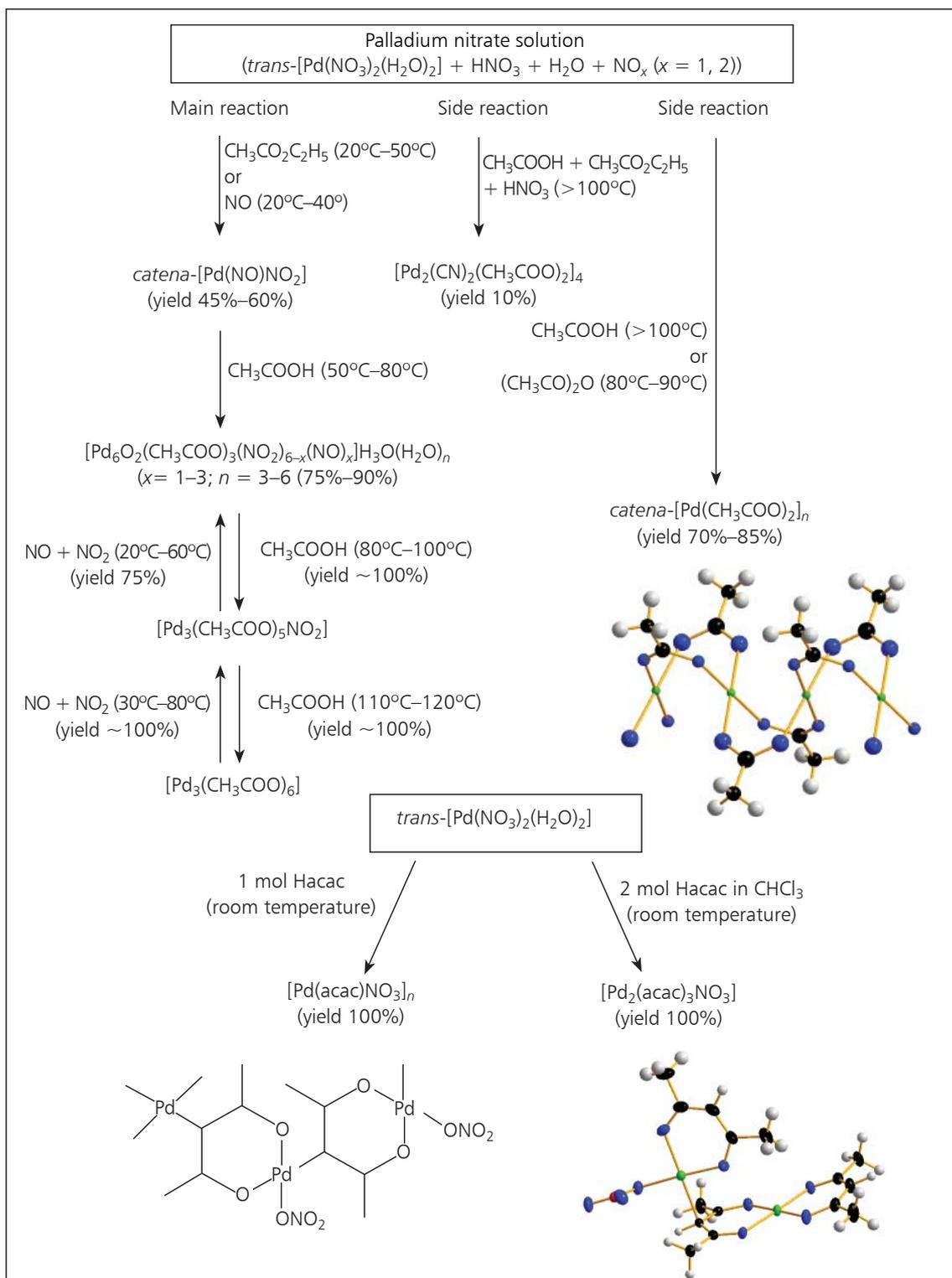


Fig. 1. Reactions of Pd(II) nitric acid solutions with acetic acid and of *trans*-[Pd(NO₃)₂(H₂O)₂] with acetylacetonone (Hacac = CH₃COCH₂COCH₃). Inserts show fragments of the corresponding crystal structures (H atoms are shown in grey, C in black, O in blue, Pd in green and N in red) and a proposed structure for [Pd(acac)NO₃]_n polymer derived from NMR and infrared spectroscopies. Yields for solid individual compounds are shown in the initial Pd(II) nitrate solution or *trans*-[Pd(NO₃)₂(H₂O)₂] (2–5) (Courtesy of Ruslan Mullagaleev (Institute of Chemistry and Chemical Technology))

laser sampling and PXRD were said to be the most appropriate methods for analysis of cultural heritage species (10).

Chemisorption of pgm on silica modified with sulfur-containing functional groups was discussed by Victoria Parfionova (Scientific Research Engineering Centre «Kristall» of the Siberian Federal University, Krasnoyarsk, Russia) and Svetlana Kozlova (Institute of Chemistry and Chemical Technology). The species $-SH$, $>S$, $-S-S-$ and $-S_n-$ at a concentration of $1.3 \times 10^{-3} \text{ mol g}^{-1}$ were used for the chemical modification of the silica surface (Figure 2). As a result, $-SH$ modified sorbents quantitatively extracted Pd(II) and Au(III) chloride complexes from 6 M aqueous hydrochloric acid solution. Di- and polysulphides extracted all pgms plus Au. Selective extraction of pgms from chloride solution was possible from 0.1 M–4.0 M HCl aqueous solutions and non-ferrous metals were extracted only at $\text{pH} > 4$ (11).

Technology and Applications of the Platinum Group Metals

Processing technology for raw materials as well as pgm production and applications were discussed between academic and industrial scientists in two corresponding sections. Oleg Belousov (Institute of Chemistry and Chemical Technology) and co-authors reported the possibilities of autoclave-based processing of pgm concentrates. Either sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4) can be used for pgm leaching in the presence of sodium sulfite (Na_2SO_3) or sodium

formate (HCOONa) respectively as reducing agents in the temperature range 120°C – 180°C for 0.5 h–4 h. Autoclave reactions and reactions with ultrasonic or microwave activation are now common practice and can be applied from microgram to ton scale. These techniques are promising as the next generation for activation of ores and concentrates.

The last session focused on applications of pgm in medicine, catalysis and materials production. Yurii Shubin (Nikolaev Institute of Inorganic Chemistry) presented recent results in the area of pgm nanoalloy preparation using soft methods such as thermal decomposition of single source precursors in the solid state. The method was actively developed during the past decade and allows various nanoalloys and supported particles to be formed under thermal treatment of solid single source precursors at 100°C – 400°C in inert (helium, argon and nitrogen) and reductive (H_2) atmosphere (12). It has been shown for Au-Ir and Au-Pd metallic systems with a wide miscibility gap that thermal decomposition of $[\text{Ir}(\text{NH}_3)_5\text{Cl}][\text{AuCl}_4]_2$ and $[\text{Pd}(\text{NH}_3)_4][\text{AuCl}_4]_2$ as single source precursors may lead to the formation of metastable $\text{Au}_{0.5}\text{Ir}_{0.5}$ nanoalloys, which can be further applied as active heterogeneous catalysts for CO oxidation or formic acid decomposition.

A novel method for the preparation of supported Pd-based catalysts was presented by Nikolay Chesnokov (Institute of Chemistry and Chemical Technology). Pd nanoparticles of diameter 2 nm–4 nm can be deposited on various carbon supports such as thermally and

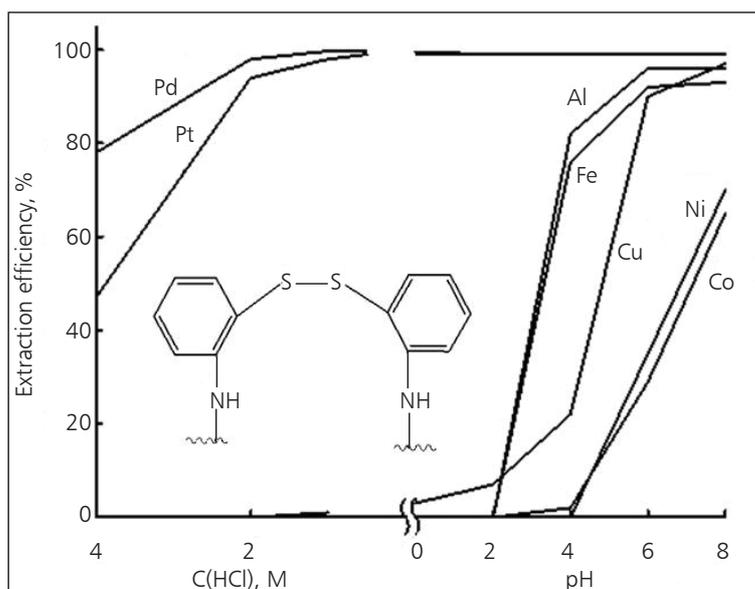


Fig. 2. Dependence of the extraction efficiency of pgms and nonferrous metals on acid concentration and pH. Extraction has been performed by silica chemically modified with disulfide groups (insert) (11) (Courtesy of Victoria Parfionova (the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University, Krasnoyarsk, Russia))

chemically activated graphite using $H_2[PdCl_4]$ solution in water-ethanol mixture.

Concluding Remarks

The Chernyaev2013 conference has shown that pgm chemistry is a still hot topic with strong practical and industrial importance. The conference has a long history with its own style and traditions, and this is expected to strengthen in the future as the conference becomes more international. The next XXI Chernyaev Conference is planned for 2016 in Yekaterinburg, Russia, and will be dedicated to the centenary of Yekaterinburg Non-Ferrous Metals Processing Plant.

Acknowledgements

The reviewers are grateful to Ruslan Mullagaleev (Institute of Chemistry and Chemical Technology) for his help with **Figure 1** as well as to Victoria Parfionova (the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University, Krasnoyarsk, Russia) for providing **Figure 2**.

References

- 1 Chernyaev2013: XX International Chernyaev Conference on Chemistry, Analysis and Technology of Platinum Group Metals: <http://conf.sfu-kras.ru/conf/chernyaev2013> (Accessed on 19th February 2014)
- 2 D. Vasilchenko, S. Tkachev, I. Baidina and S. Korenev, *Inorg. Chem.*, 2013, **52**, (18), 10532
- 3 R. F. Mulagaleev and S. D. Kirik, *Russ. J. Appl. Chem.*, 2010, **83**, (12), 2065
- 4 S. D. Kirik, R. F. Mulagaleev and A. I. Blokhin, *Acta Crystallogr. C.*, 2004, **60**, 449
- 5 S. P. Khramenko, E. A. Bykova, S. G. Gromilov, M. R. Gallyamov, S. G. Kozlova, N. K. Moroz and S. V. Korenev, *Polyhedron*, 2012, **31**, (1), 272
- 6 S. P. Khramenko, S. V. E. Korenev, L. V. Ivanova, V. A. Vostrikov and N. G. Prudnikova, Krasnoyarsk Non-Ferrous Metals Plant, 'Method of Palladium Acetate Production', *Russian Patent 2,344,117*; 2007
- 7 R. F. Mulagaleev and S. D. Kirik, Institute of Chemistry and Chemical Technology SB RAS, 'Method of Palladium Propionate', *Russian Patent 2,425,023*; 2009
- 8 A. V. Belyaev, *J. Struct. Chem.*, 2003, **44**, (1), 29
- 9 V. A. Emel'yanov, M. A. Fedotov, A. V. Belyaev and S. V. Tkachev, *Russ. J. Inorg. Chem.*, 2013, **58**, (8), 956
- 10 L. P. Zhitenko, V. P. Obrezumov, S. K. Bukhryakova, L.

D. Gorbatova, T. G. Il'yusha, T. P. Zemlyavko and I. A. Khabeev, *Inorg. Mater.*, 2009, **45**, (14), 1511

- 11 A. K. Trokhimchuk, N. A. D'yachenko, A. V. Leginchuk, V. N. Losev, *Ukrainian Chem. J.*, 2004, **70**, (1), 34
- 12 Y. Shubin, P. Plyusnin and M. Sharafutdinov, *Nanotechnology*, 2012, **23**, (40), 405302

The Reviewers



Kirill Yusenko studied chemistry at the Novosibirsk State University, Russia, and received his PhD in 2005 from the Nikolaev Institute of Inorganic Chemistry in the area of coordination and material chemistry of pgms. After a year as a postdoctoral researcher at the University of Hohenheim, Stuttgart, Germany, he spent several years as a researcher at the Ruhr-University Bochum, Germany. Since 2012 he holds a position at the Department of Chemistry, University of Oslo, Norway. His scientific interests are focused on the chemistry of pgms and nanomaterials based on metallic particles, thin films and porous coordination polymers as well as solid-state chemistry of pharmaceutical materials. He attended Chernyaev2013 as a plenary speaker.



Sergey Metelitsa studied chemistry at the Krasnoyarsk State University, Russia, and received his PhD in 2009 from the Siberian Federal University (SFU) in Krasnoyarsk, Russia, in the area of luminescence analysis of pgms. After this he worked at the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University in Krasnoyarsk, Russia, for 3 years. During this period, he studied the complexation of pgms and other non-ferrous metals with inorganic oxides as active supports. Now he is a permanent researcher at the SFU. His scientific interests are focused on the analysis and coordination chemistry of pgms as well as environmental chemistry. He was the academic secretary for Chernyaev2013.



Vladimir Losev studied chemistry at the Krasnoyarsk State University, Russia, and received his PhD and further Doctoral degrees in Chemical Sciences in 2007 from the Scientific Research Engineering Centre «Kristall» of the Siberian Federal University in Krasnoyarsk, Russia. Currently he is a professor of analytical chemistry at the SFU. His scientific interests are focused in the area of analytical chemistry, especially spectroscopic analysis of pgms in environmental and industrial objects. He was the chairman of Chernyaev2013 and head of the local organising committee.