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Origin and development of coordination chemistry in Poland—Introductory remarks

Zofia Stasicka[a], Józef J. Ziółkowski[b,*]

[a] *Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland*
[b] *Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland*

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Abstract

The origin of coordination chemistry in Poland is reviewed and two main centres of its development in Kraków and in Wrocław are briefly characterized. Coordination chemistry in Poland is usually associated with the name of Bogusława Jeżowska-Trzebiatowska (1908–1991), Professor of Chemistry at Wrocław University, generally recognized as the founder of the Wrocław School of Coordination Chemistry.

The history of coordination chemistry which started with Professor Wiktor Jakób in Lwów will be described with particular emphasis from its initiation in Lwów and continuation in Kraków (Jagiellonian University) and further development at the University of Wrocław in Wrocław. Authors in this volume, from research centres other than Wrocław and Kraków present progress in inorganic and coordination chemistry in those other regions of Poland.

Keywords: Coordination chemistry in Poland

1. Origin of coordination chemistry at Lwów Technical University

It was only 30 years after Alfred Werner (Nobel Prize in chemistry in 1913) published his revolutionary theory propagating the idea of two types of valence existing in a large family of compounds (named later coordination compounds), when Dr. Wiktor Jakób, a young analytical chemist, became an associate professor of inorganic chemistry and was appointed the head of the Department of Inorganic Chemistry at the Technical University in Lwów (Poland). This was a real challenge, because the department must have been organized from the very beginning. Taking this challenge W. Jakób decided to focus his studies on the quite new field of inorganic chemistry, which was at that time coordination chemistry. This date, i.e. September 1926 may thus be assumed as the date of birth of coordination chemistry in Poland (Fig. 1).

The research area initiated by Wiktor Jakób attracted the attention of a group of young, talented students, some of which later became outstanding scientists, well-known in Poland, such as Włodzimierz Trzebiatowski and Bogusława Jeżowska (later Jeżowska-Trzebiatowska) and in Ukraine (Cyryl Michalewicz) (Fig. 2).

The earliest papers published by Jakób and his co-workers were focused on chemical [1–11] and electrochemical properties [12,13] of coordination compounds of such elements as chromium, vanadium, molybdenum, tungsten and rhenium. Rhenium was then quite newly discovered (W. Noddack, I. Tacke, 1925) and the investigation of rhenium chemistry carried out by Jakób and Jeżowska [5–7,19] showed its new properties, especially the oxidation number V, which was unexpected by the rhenium discoverers, who originally were opposed to these observations. After additional experiments, made by B. Jeżowska and longer discussion, W. Noddack and I. Tacke-Noddack accepted the arguments of the Polish scientists.

* Corresponding author. Tel.: +48 71 3757 356; fax: +48 71 3757 356.
E-mail address: jjz@wchuwr.chem.uni.wroc.pl (J.J. Ziółkowski).

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Fig. 1. Wiktor Jakób (1886–1971).

2. Revival of coordination chemistry and its development at the Jagiellonian University

The Second World War suddenly interrupted and for a long time, the research of W. Jakób and his students. Afterwards the Polish scientists had to move from Lwów to other places and W. Jakób again had to organize the Department of Inorganic Chemistry, first at the Technical University in Gliwice and next at the Jagiellonian University in Kraków. There for a second time he organized a group of students to start again the research on coordination chemistry.

From the beginning of his scientific career till his death (1971) W. Jakób carried out the study of structure, electrochemistry, spectroscopy, thermal reactivity and photochemistry of coordination compounds. His main interest was focused on complexes of transition metals, such as tungsten, molybdenum, chromium, manganese and cobalt.

One subject area included in W. Jakób's studies consisted of the spectroscopy and photochemistry of coordination compounds, which began as early as the 1920s [13] and was considerably developed later in collaboration with Z. Jakób [14], A. Samotus and Stasicka [15–19] (Fig. 3) and Senkowski [20–23]. The results showed new photochemical pathways proceeding in the octacyanometallates of molybdenum and tungsten [15–19] and in nitrosylpentacyanomanganates [20–23]. The research included chemical and physicochemical experiments, but some of the spectroscopic and mechanistic problems were solved in cooperation with theoretical chemists [19,20].

The subject matter included mostly the isoleptic or mixed ligand cyanide complexes, characterized by a large vari-

Fig. 2. First co-workers of W. Jakób: from the left C. Michalewicz, B. Jeżowska and W. Trzebiatowski (Lwów 1934).

Fig. 3. W. Jakób and two of his students and co-workers A. Samotus (on the left side) and Z. Stasicka (Kraków 1964).

ety of coordination numbers, especially those unusually high [14–19]. Among the systems most intensively studied by W. Jakób and his students were cyanide complexes containing which also contained the nitrosyl ligand. In this subject, not only photochemistry but also electrochemistry and chemical behaviour were investigated, mostly in collaboration with Senkowski [20–23], Hejmo and Kanas [24–26]. The results showed one of the first pathways of activation of small gaseous molecules, such as NO and O_2 [24–26].

This short review of W. Jakób's activity shows that he was a pioneer in many fields which are of relevance to contemporary science and preceded the development in such subject areas of coordination chemistry as photochemistry, correlation between structure and reactivity, complexes with high coordination numbers, versatility of cyanide, nitrosyl and other ligands, activation of nitric oxide, molecular oxygen and other small gaseous molecules.

After W. Jakób's death (1971) his research was continued and developed by his students and co-workers, which gave rise to the two main centres of coordination chemistry in Poland at the Jagiellonian University of Kraków and in the University of Wrocław.

The coordination centre in Kraków was focused on chemical and photochemical activity as well as the application of coordination compound. Recent research includes mainly: structural [27–37], mechanistic [38–50] and kinetic aspects [51–55], their role and relevance in biology, medicine [56–64] and environment [65–72], their use in homogeneous and heterogeneous photocatalysis [71–74] and their contribution to the production of new materials functioning as information carriers [75–79], chemical logic gates and chemosensors [80,81].

3. Development of coordination chemistry at the Wrocław University

After the Second World War, most of the Polish scholars from Lwów (today's Lviv), both from the Jan Kazimierz University and from Lwów University of Technology, moved west. Some, like Professor Wiktor Jakób, settled in Kraków; others, like Professor Włodzimierz Trzebiatowski and his wife, a student and co-worker of Professor Jakób's, Dr. Bogusława Jeżowska-Trzebiatowska, moved further west, to Wrocław (former Breslau).

Wrocław emerged from the war completely devastated, but soon after the military operations ended, a group of academic staff and students from Lwów arrived in the city, which was still burning, and set out to organize a University and a University of Technology. Professor Trzebiatowski and Dr. Jeżowska-Trzebiatowska (professor of chemistry from 1954) were those who established inorganic chemistry research centres in Wrocław—he at the University of Technology, concentrating on solid-state chemistry and crystallography; she at Wrocław University, initially continuing studies on the chemistry of rhenium, which she had begun at Lwów, and then extending her explorations to other metals and expanding analytical and kinetic studies through the use of modern experimental and theoretical methods in coordination chemistry (Fig. 4).

In 1951 Dr. Jeżowska-Trzebiatowska began laying foundations for a school of chemistry at Wrocław University's Faculty of Mathematics, Physics and Chemistry. The early publications, in the 1950s, concerned primarily the reaction kinetics and synthesis of compounds of manganese (Maria Wrońska, Jadwiga Nawojska) and rhenium (Stanisław Wajda, Helena Przywarska-Boniecka,

Fig. 4. Professor B. Jeżowska-Trzebiatowska in the laboratory (1961).

Jadwiga Danowska and later on Walter Wojciechowski) [82–86].

In 1955 Professor Jeżowska-Trzebiatowska, together with Lech Pajdowski [87,88], embarked on research into the chemistry of vanadium (polynuclear complexes) and the reaction kinetics of ferrates (Maria Wrońska, Jan Biernat) [89] (Fig. 5).

The late 1950s saw the launch of the investigation of the chemistry of uranium, for the first time, in Poland, and the first applications of radioactive isotopes in studies of the kinetics and structure of transition metal coordination complexes.

The first papers on the coordination chemistry and spectroscopy (UV–vis, IR) of uranium(VI) (Adam Bartecki, Bogusław Kędzia and Władysław Kąkołowicz), U(IV) and U(III) (Krystyna Bukietyńska-Słopecka, Janusz Drożdżyński) [90–93] were published towards the end of the 1950s. Somewhat later, investigations of the magnetic and spectroscopic properties of f-electron elements, not only actinides but also lanthanides, were started (Janina Legendziewicz, K. Bukietyńska, J. Drożdżyński) [94,95]. In subsequent years that research area was considerably broadened and has continued to be explored to this day. The earliest applications of radioisotopes in kinetic studies (radioisotope exchange) and structural investigations of rhenium(IV) complexes (S. Wajda, Florian Pruchnik) [96] and pentacyanonitrosyl transition metal complexes (Józef J. Ziółkowski, Antoni Keller) [97–100] were the subject-matter of publications in the early 1960s. Around the same time, the first studies involving the use of X-rays and then γ(^{60}Co) radiation in the field of the radiation chemistry of transition metal oxyanion solutions (Jerzy Kaleciński) [101] and subsequently transition metal complexes (Elżbieta Kalecińska) [102] began.

As early as the mid-1950s, at the initiative of Professor Jeżowska-Trzebiatowska, the first publications describing the magnetic properties of transition metal complexes appeared,

Fig. 5. Professor B. Jeżowska-Trzebiatowska with her co-workers and Professor K.B. Yatsimirskii (1958).

Fig. 6. Professor B. Jeżowska-Trzebiatowska with co-workers—J.J. Ziółkowski and J. Drożdżyński standing by the first Gouy, balance in Poland (1959).

shortly after the first Gouy balance in Poland had been built at Wrocław (Fig. 6).

A large number of papers describing the magnetic (dia-, para-, ferro- and antiferromagnetic) properties of new transition metal complexes were published after 1958 (S. Wajda) [103], and such investigations have been developed and continued to this day (W. Wojciechowski, Jerzy Mroziński, Mikołaj Rudolf) [104–106] (Fig. 7).

Crystallographic, magnetochemical, spectroscopic and theoretical studies of transition metal complexes with a metal–oxygen–metal core were the object of Professor Jeżowska-Trzebiatowska particular interest and led to the formulation of the oxygen bond theory, which explained the magnetic properties of such complexes (W. Wojciechowski, Tadeusz Głowiak) [107–110]. In the early 1970s Professor Jeżowska-Trzebiatowska established a Department of Chemistry at Wrocław University, and it soon became one of the leading centres in Poland for the training of chemists and for fundamental research. A major role was played by the Summer Schools on Coordination Chemistry (the first one held in 1964; the latest, fifteenth, in 2004), known throughout Europe and beyond, which have become an international platform for the exchange of knowledge, contributing greatly to the development of international collaboration in the field of broadly defined coordination chemistry. In recognition of Polish achievements in coordination chemistry and Professor Jeżowska-Trzebiatowska's personal contribution, the international community of coordination chemists entrusted her with the task of organizing the 13th International Conference on Coordination Chemistry (XIII ICCC) in 1970, the first such congress in Eastern Europe.

That was a Herculean task, but with the help of the Kraków chemists the XIII ICCC was successfully organized in Kraków and Zakopane in September 1970. The conference was a milestone in the development of coordination chemistry, not only in Wrocław but in all of Poland.

The last three decades of the twentieth century have been marked primarily by a significant improvement in working

Fig. 7. Professor A.A. Greenberg, outstanding Russian coordination chemist (first from the left) with Professors B. Jeżowska-Trzebiatowska and W. Trzebiatowski.

Fig. 8. Professor B. Jeżowska-Trzebiatowska and Professor J.J. Ziółkowski—15th anniversary of Institute of Chemistry (1984).

conditions (new facilities built in the years 1970–2005) and substantial upgrading of laboratory equipment (new instruments, such as ESR, 300 MHz and 500 MHz NMR, CD-X-Ray cameras, GC–MS, ESI–MS, ICP, FTIR, Raman, luminescence spectrometers, and so on, and so forth).

These facts and the constantly intensified international collaboration have consolidated the high esteem enjoyed by Poland's coordination chemistry centres (Wrocław, Kraków, Poznań, Toruń, Warsaw, Gdańsk and other universities) and especially by Wrocław (Faculty of Chemistry, Wrocław University and Faculty of Chemistry, Wrocław University of Technology) (Fig. 8).

During the past twenty years coordination chemistry in Wrocław has focused, as before, on research into the synthesis of new coordination and organometallic compounds, studies of their electron and molecular structures and investigations of their reactivity in the context of both the biological role of metal complexes and their function as catalysts for organic reactions. In recent years, these three areas of fundamental research have become increasingly oriented towards the practical applications of coordination and organometallic chemistry in bioinorganic and biomedical chemistry (Henryk Kozłowski, Lechosław Latos-Grażyński, Florian Pruchnik, Piotr Sobota, Janina Kuduk-Jaworska) as well as catalysis (Józef J. Ziółkowski, Anna M. Trzeciak, Florian Pruchnik, Piotr Sobota, Teresa Szymańska-Buzar, Antoni Keller) and chemistry of new materials (nanocatalysis).

Worth mentioning within the above area of research currently pursued at the Faculty of Chemistry, Wrocław University, by students and collaborators of Professor Jeżowska-Trzebiatowska's, are the following.

Particularly notable in this area of coordination chemistry are studies initiated and developed by Professor Henryk Kozłowski and his team (Małgorzata Jeżowska-Bojczuk, Wojciech Bal, Teresa Kowalik-Jankowska), which relate to the following topics:

- The influence of metal ions (Cu(II), Ni(II), Zn(II), Al(III) and Fe(III)), on the structure and functions of biomolecules and their subunits (amino acids, peptides, aminosugars, nucleotides, antibiotics, hormones, fragments of major component proteins of insoluble amyloid fibrils in neurodegenerative diseases).
- Interaction of aminoglycosides and their copper(II) complexes with nucleic acids in the presence of hydrogen peroxide. Implications for the toxicity of such drugs.
- The effect of anticancer drugs (both potential and in use) on the structure and functions of proteins with a focus on understanding their toxicity and distribution in the organism.

The above topics are the subject of ongoing studies, amply reflected in the following recent publications: [111–125].

Advanced studies in the chemistry of porphyrins and metalloporphyrins are conducted by Lechosław Latos-Grażyński and his co-workers. The main research areas include synthetic, structural and mechanistic investigations of new classes of core-modified and expanded porphyrins. The mechanistic studies have led to the identification of intermediate forms in Fe(II) porphyrin oxidation and dioxygen insertion into the Fe–C bond, and the discovery of an unorthodox structure of ditelluraporphyrin [126–141].

Research in the area of small molecule activation by organometallic complexes, initiated by Bogusława Jeżowska-Trzebiatowska, has been pursued by Piotr Sobota and his co-workers. The main emphasis in these studies lies in the correlation between electron and molecular structures of complexes and their reactivity, including catalytic reactivity. Based on X-ray studies, the structure of catalyst precursors has been determined and methods for the synthesis of new-generation supports for olefin polymerization catalysts have been developed [142–154].

Extensive studies of various aspects of coordination chemistry and molecular metal wires, organometallic chemistry and homogenous catalysis, and some aspects of bioinorganic chemistry are carried out by Florian Pruchnik and his co-workers [155–165].

The first text on organometallic chemistry to be published in Poland was, *Organometallic Chemistry of the Transition Elements*, published in English, which together with two others, published in Polish, were authored by Pruchnik [166,167] and Pruchnik et al. [168].

The broad field of transition metal coordination chemistry, organometallic chemistry and metal complex catalysis with homogenous, heterogenized and nanometal catalysts is the area investigated by Józef J. Ziółkowski and his co-workers (Anna M. Trzeciak, Teresa Szymańska-Buzar, Antoni Keller and Monika Moszner). The studies, started in the early 1970s with investigation of cobalt and molybdenum coordination chemistry with regard to catalytic oxidation and epoxidation, have in recent years been extended to the organometallic chemistry of rhodium relating to catalytic hydroformylation, hydrogenation, isomerization and polymerization; organometallic compounds of tungsten and molybdenum as catalysts of olefin metathesis, ROMP reaction and some aspects of photocatalysis; and finally organometallic chemistry of palladium as a catalyst for metoxycarbonylation and Heck, Suzuki and Sonogashira reactions involving the use of molecular Pd(II) complexes as well as Pd(0) colloids [169–189].

Investigation of the physical chemistry of lanthanides and structural studies of ligand systems are conducted by Janina Legendziewicz and her co-workers (Jacek Gliński, Grażyna Oczko).

The field of their research covers electron-relaxation processes in lanthanide systems; the use of lanthanide ions as models and spectroscopic probes in biological applications; and the chemistry, structure and spectroscopy of lanthanide compounds [190–199].

The chemistry of trivalent uranium has, for a long time, been the main research interest of Janusz Drożdżyński and his co-worker Mirosław Karbowiak. Their investigation encompasses the synthesis and the structural, magnetic and spectroscopic characterization of new U(III) compounds and some of their Np(III) and Nd(III) analogues [200–206].

The broad application of EPR spectroscopy in coordination chemistry studies of transition metal compounds and their magnetic interactions in transition metal compound–free radical systems is demonstrated in the work carried out by Julia Jezierska and Adam Jezierski.

Their investigations include interactions of free radicals in natural materials, biological membranes and humic acids.

EPR spectroscopy has also been successfully applied in studies of the coordinating properties of different functional groups in synthetic polymers [207–213].

Studies of the magnetic properties of transition metal compounds, initiated by Bogusława Jeżowska-Trzebiatowska, have been continued and further developed by Jerzy Mroziński. His recent work comprises the investigation of new magnetic materials and correlation of low-temperature magnetic properties with magnetic interaction propagated by multiatom bridges [214–219].

4. Conclusion

The above listing of examples of research in the area of coordination chemistry and related chemical subdisciplines at Wrocław University is far from complete.

Coordination chemistry at Wrocław University of Technology has only been mentioned in passing.

Also, coordination and organometallic chemistry studies at research centres other than Wrocław and Kraków, such as the Adam Mickiewicz University in Poznań, the University of Warsaw, Warsaw University of Technology, the University of Gdańsk, the University of Łódź, the University of Toruń, the University of Opole and the University of Silesia in Katowice—have not been covered in this article.

This will be partially covered in the review articles included in this issue. However, since the authors are recruited mainly from the University of Wrocław and Jagiellonian University in Kraków we certainly recognize other regions of Poland as strong research centres in inorganic and coordination chemistry. First of all, the large group of inorganic chemists from Wrocław University of Technology should be mentioned where also under the inspiration of Professor Jeżowska-Trzebiatowska, excellent studies on the spectroscopy of coordination compounds (Professor Adam Bartecki, Professor Bogusła Kędzia and recently Professor M. Cieślak–Golonka) as well as structural and theoretical chemistry (Professor W. Wojciechowski) have been reported.

One should also mention the implementation of coordination chemistry into the hydrometallurgy of copper in the copper industry and the development of supramolecular chemistry. Spectacular development of coordination and organometallic chemistry can be observed at the Adam Mickiewicz University in Poznań. In this issue of CCR there are three review papers which properly describe topics and achievements on coordination, supramolecular and organosilicon chemistry developed in Poznań (Professors W. Radecka–Paryzek, Bogdan Marciniec and Lechosław Łomozik). Extremely valuable and industrially important progress in organosilicon chemistry has been achieved by Professor B. Marciniec especially in the scope of synthesis and new metal complex catalyzed reactions of potential industrial application.

The organometallic chemistry of both main group and transition group elements has been developed at Warsaw University of Technology (Professor Stanisław Pasynkiewicz). Their contribution to organoaluminum chemistry is particularly important.

Of course, the geographical location of inorganic and coordination chemistry is not limited to Wrocław–Kraków–Poznań and Warsaw. Very strong and active research groups can be found in Gdańsk (University of Gdańsk), Toruń (M. Copernicus University in Toruń, Prof. A.A. Grodzicki and E. Szłyk), University of Opole, Silesian University in Katowice and other Universities.

In conclusion, it should be recognized that coordination chemistry in Poland developed extremely rapidly after the Second World War and enjoys extensive contact with other leading research centres in the world. This was demonstrated by the increasing contribution of polish chemists to the world progress in coordination chemistry and related sciences.

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