



Photo courtesy of the late Marjan Smerke

Dedicated to the memory of the late Prof. Dr. Boris Žemva (1940–2023)

The passing of Professor Boris Žemva, known simply as Boris among his colleagues, on November 2, 2023 marks the loss of one of the most influential figures in modern inorganic fluorine chemistry. Over nearly five decades of research, he shaped several fundamental directions in the chemistry of noble gases, high-oxidation-state fluorides, and coordination chemistry involving weak ligands. Through his scientific insight, experimental mastery, and dedication to mentoring younger generations, he left a legacy that extends far beyond his publications and discoveries.

The development of fluorine chemistry in Slovenia forms a remarkable scientific lineage that spans several generations. The foundations were laid in the 1950s and 1960s by Prof. Jože Slivnik at the Jožef Stefan Institute, at a time when the chemistry of noble gases had only just emerged as a new frontier in inorganic chemistry. In 1962, when Neil Bartlett demonstrated that xenon could form compounds, the prevailing view of noble gases as chemically inert elements was overturned almost overnight. Slivnik's group was among the first in the world to pursue this new chemistry, successfully synthesizing xenon fluorides under elevated temperatures and pressures.

It was into this pioneering research environment that Boris entered in 1965 when Slivnik invited him to join the laboratory at the Jožef Stefan Institute. Born in Ljubljana in 1940 and educated at the University of Ljubljana, Boris had already shown a remarkable determination to pursue chemistry. As he later recalled, even as a high-school student he knew with certainty that chemistry would define his future.

Under Slivnik's mentorship, Boris completed his master's and doctoral studies, focusing on the synthesis and reactivity of xenon fluorides. His doctoral work on reactions between xenon and fluorine under pressure not only contributed to improved synthetic methods for XeF_2 , XeF_4 , and XeF_6 but also provided him with the experimental confidence and technical expertise required for one of the most experimentally demanding branches of inorganic chemistry.

A defining stage of his scientific development occurred during his collaboration with Prof. Neil Bartlett at the University of California, Berkeley, where he worked as a Fulbright Scholar and later as a Visiting Miller Research Professor. The partnership between Bartlett and Boris proved extraordinarily fruitful and helped establish several fundamental concepts in the chemistry of high-oxidation-state fluorides and noble-gas compounds.

Following the sudden death of Prof. Jože Slivnik in 1983, Boris assumed leadership of the laboratory at the Jožef Stefan Institute. In doing so he inherited not only a research group but also a highly specialized tradition of experimental fluorine chemistry. Under his guidance the laboratory continued to develop as an internationally recognized center for synthetic and structural fluorine chemistry. He also established X-ray diffraction facilities that became essential for structural characterization of the complex compounds produced in the laboratory.

The chemistry that fascinated Boris was never routine. Fluorine chemistry—particularly the chemistry of

noble-gas fluorides and transition-metal fluorides in high oxidation states—represents one of the most experimentally demanding domains of inorganic chemistry. Many of the compounds involved are thermodynamically unstable, extremely reactive, and hazardous to manipulate. This is illustrated by a commentary from Nobel Laureate Prof. Roald Hoffmann, who wrote in *American Scientist* about the synthesis of $[\text{XeF}_5][\text{AgF}_4]$: »And Žemva used Kr^{2+} (in KrF_2) to react with AgF_2 in anhydrous HF in the presence of XeF_6 to make $\text{XeF}_5^+\text{AgF}_4^-$. What a startling list of reagents!« Work with such systems requires not only exceptional technical competence but also a high degree of experimental intuition and courage. Boris possessed both in abundance.

Among his most influential contributions were the synthesis and structural characterization of transition-metal fluorides in unusually high oxidation states, including metastable compounds such as AgF_3 , NiF_4 , NiF_3 , and CuF_3 . These systems represent some of the most powerful oxidants known in chemistry. Their preparation required innovative strategies involving the most potent oxidizing agents, such as KrF_2 , and tuning of the Lewis acidity/basicity of the anhydrous HF, in which solvated cationic Ag^{III} and Ni^{IV} species exhibit extraordinary oxidizing power—so strong that even molecular oxygen and xenon act as reducing agents under these conditions.

He also investigated the Lewis basicity, that is, the fluoride-donor properties of noble-gas fluorides in reactions with various Lewis acids. These studies led to numerous new noble-gas compounds such as $[\text{Xe}_2\text{F}_{11}]_2[\text{NiF}_6]$, $[\text{XeF}_5][\text{CrF}_4]$, $\text{XeF}_2 \cdot 2\text{CrF}_4$, and $\text{XeF}_2 \cdot \text{CrF}_4$. The latter compound, XeCrF_6 , represented a structural model for the still unknown crystal structure of the first noble-gas compound, XePtF_6 , and its structure has therefore appeared in various textbooks and review articles.

Equally insightful were Boris's extensive studies of the coordination chemistry of noble-gas fluorides. His group systematically investigated metal complexes containing XeF_2 as a ligand and synthesized and structurally characterized more than forty new compounds in this area. These studies included the first example of homoleptic XeF_2 coordination of a metal cation, the first coordination complex in which XeF_4 acts as a ligand toward a metal ion, and the first coordination compound involving KrF_2 bound to a naked metal cation. These discoveries significantly expanded the structural and conceptual landscape of noble-gas chemistry.

Beyond noble-gas chemistry, Boris's creative work also extended into coordination chemistry of weakly coordinating anions and weak donor ligands. Beginning with the synthesis and structural characterization of the first

coordination complex in which hydrogen fluoride acts as a ligand to a metal cation, he and his collaborators reported numerous studies on metal complexes containing HF as well as on salts containing poly(hydrogen fluoride) anions. At the same time, they also explored the chemistry of weakly coordinating anions and lanthanide systems, revealing a rich structural diversity across a wide range of coordination environments.

The impact of his fundamental research is perhaps most clearly reflected in its presence in modern inorganic chemistry textbooks. Several of the most widely used textbooks, including *Inorganic Chemistry* by C. E. Housecroft and A. G. Sharpe, *Shriver & Atkins' Inorganic Chemistry* by P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong, and *Inorganic Chemistry* by G. L. Miessler, P. J. Fischer, and D. A. Tarr, depict crystal structures and describe synthetic procedures for compounds discovered or investigated in his laboratory. Only a relatively small number of scientists can claim that students around the world encounter their research results while studying inorganic chemistry; Boris unquestionably belongs to this select group.

The excellence of his research was recognized through numerous prestigious distinctions, including the Humboldt Research Award in 1999, the Ambassador of Science of the Republic of Slovenia Award in 2001, the ACS Award for Creative Work in Fluorine Chemistry in 2006 and the Zois Prize for Lifetime Achievement in 2011, the highest scientific accolade in Slovenia.

Although his work was primarily fundamental in nature, Boris also applied his expertise in handling highly reactive fluorides to the synthesis and study of fluorinated materials. Using highly reactive fluorine compounds, his research group prepared various fluorinated materials, whose physical and electrochemical properties were investigated through international collaborations. This led, among other things, to an industrial collaboration and an international patent.

At the heart of Boris's scientific success was his distinctive laboratory philosophy. Unlike many senior scientists whose work gradually becomes detached from the experimental bench, he remained a deeply hands-on experimentalist throughout his career. He worked in the laboratory alongside his students and collaborators, often participating directly in the design and execution of experiments. When asked what should be emphasized in his nomination for the ACS Award for Creative Work in Fluorine Chemistry, he answered with characteristic modesty that perhaps the most relevant fact was simply that he had spent much of his career working in the laboratory himself.

This experimental engagement also defined his approach to mentorship. His influence as a teacher and mentor extended well beyond textbooks. Throughout his career he devoted considerable effort to the careful transmission of knowledge and the generous sharing of his experimental experience and enthusiasm with younger generations. Conversations with him rarely resembled formal meetings. We could enter his office discouraged by a failed experiment or a seemingly unsolvable research problem, yet leave with renewed motivation and a clearer understanding of how to proceed. Rather than imposing solutions, he guided us toward discovering answers by ourselves, cultivating both independence and confidence. His mentorship qualities were recognized with the Mentor of the Year Award in 2012.

His dedication to research was legendary. An unexpected experimental result late at night could easily prompt him to appear in the laboratory within minutes, eager to examine the data and discuss its implications. Chemistry, for him, was never merely a profession—it was a way of life. Outside the laboratory, he found inspiration in the

Slovenian mountains, where he was an enthusiastic hiker, and enjoyed sharing good company over a glass of fine wine.

Equally important were the values he transmitted to younger colleagues: intellectual curiosity, persistence in the face of experimental challenges, and respect for careful laboratory work. He often expressed his philosophy in simple terms, stating that genuine interest is the fundamental prerequisite for becoming a good chemist.

Through his mentorship he trained a generation of chemists who continue to develop the fields to which he devoted his life. In this sense, the scientific lineage that began with Slivnik continues through Boris and into the present generation of fluorine chemists.

Today his scientific legacy remains present not only in the compounds he discovered and the publications he authored, but also in the laboratories, collaborations, and research traditions he helped build. For those of us who had the privilege of working with him, it remains a profound honor to say that we once learned fluorine chemistry under the guidance of Professor Boris Žemva.

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