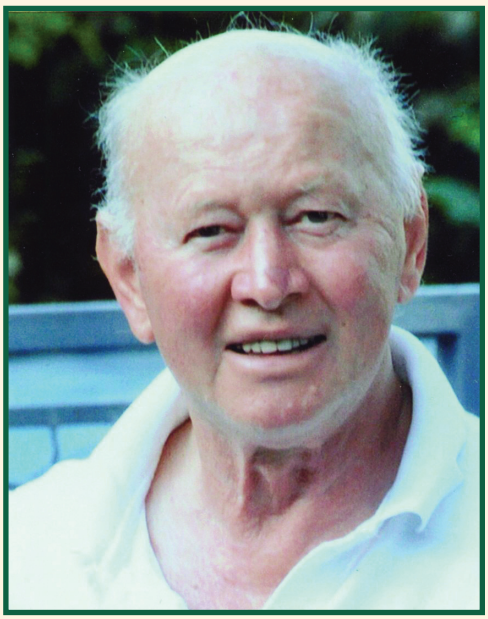
Acta Chimica Slovenica

Memorial Issue



Dedicated to the memory of Prof. Dr. Jurij Vinko Brenčič (1940–2013)

This issue of *Acta Chimica Slovenica* is a tribute to the contributions and influence that my dear friend, Prof. Jurij V. Brenčič, had on the field of the coordination chemistry of chromium, molybdenum and tungsten and the inorganic chemistry in general. The issue which has been put together by his lifelong colleagues and former students covers a range of topics of which some are related to his field of research.

Jurij V. Brenčič was born on February 18, 1940, in Ptuj and died on June 28, 2013, in Ljubljana. His early childhood was spent in Titovo Užice in Serbia, where the Brenčič family was exiled to at the beginning of WW2. In spring 1945, the family returned to Ptuj, where Jurij attended the local primary school and later the upper secondary school. He was fascinated with chemistry since his first encounter with it. It is no surprise that he followed his childhood dream and in 1958, he enrolled in the Department of Chemical Technology at the Faculty of Natural Sciences and Technology at University of Ljubljana, in order to study chemistry. Not only was he an excellent student, he was soon engaged as a demonstrator in the inorganic chemistry laboratory practical. He finished his undergraduate studies in spring 1962 and a few months later obtained a position as a teaching assistant at the same institution. In June 1965 he finished his master's thesis *The Influence of the Atmosphere on the Reactions Between the $CaCO_3$–MoO_3, $BaCO_3$–MoO_3, $BaCO_3$–WO_3, Pb-O–TiO_2 and $PbCO_3$–TiO_2 Systems*, for which he received the Prešeren Award. In September 1967, he joined a research group of Prof. F. A. Cotton, one of the twentieth century's most creative and influential inorganic chemists, at Massachusetts Institute of Technology in Cambridge, USA, as a Samuel Robin Foundation fellow. It was during his two-year stay at the Massachusetts Institute of Technology that he became involved in the molybdenum coordination chemistry. As his younger colleague, I heard him talking about that period on many occasions. After working late hours in the laboratory and countless fruitless attempts to grow good-quality single-crystals of a compound containing the $[Mo_2Cl_8]^{4-}$ ion, he finally succeeded. The X-ray structure analysis of tiny purple crystals, obtained from the reaction of molybdenum(II) acetate with hydrochloric acid, unambiguously confirmed the existence of a novel dinuclear molybdenum species with adjacent metal ions at an extremely short distance, shorter than in the bulk metal itself, *i.e.*, 2.13 Å. This distance was interpreted in terms of a quadruple metal–metal bond. Today it seems incredible, but Jurij's discovery, as stated by Prof. F. A. Cotton in his *Multiple Bonds Between Metal Atoms*, was a critical breakthrough in the evolution of the Mo_2^{4+} chemistry. After Jurij defined the exact conditions for the transformation of molybdenum(II) acetate, a decade of virtually exponential growth of the field of the M–M multiple bonds commenced. By July of 1968, a report on the preparation and X-ray verification of the first of the several compounds containing the $[Mo_2Cl_8]^{4-}$ ion, was submitted to *Inorganic Chemistry*. Just two years later, Jurij published four more papers on compounds of this type in *Inorganic Chemistry*. In October 1969, following his return from the USA, he completed his Ph.D. degree with the thesis *Study and Structures of a Series of Chlorodimolybdates(II)* and started his independent academic career at the Department of Chemistry and Chemical Technology at University of Ljubljana. He rose to the rank of Full Professor in 1981. Over the intervening 35 years, he taught courses on general chemistry, inorganic chemistry and coordination chemistry to generations of students studying chemistry and pharmacy. He was also a very supportive and encouraging mentor. Under his leadership, 50 students graduated, 9 postgraduate students completed their master's and 5 their doctoral theses. He served as a member of many committees and advisory boards, and for over a decade, he was also the head of the Inorganic Chemistry Group. Jurij spent his entire career at the Department of Chemistry and Chemical Technology at University of Ljubljana and retired as Professor Emeritus in 2007.

Jurij was a prominent scientific educator and textbook author. His *General and Inorganic Chemistry* ('Splošna in anorganska kemija'), co-authored with his long-time colleague, also late

Prof. Franc Lazarini, published in 1984, was the first university chemistry textbook in Slovenian. The textbook underwent several editions and continues to remain a standard text for the Slovenian first-year students of chemistry and related fields of study. The book has acquired unexpected fame, with the students referring to it simply by the last names of either of the two authors. Jurij and Franci also shared a deep concern for the education of high-school students. They co-authored two high-school textbooks, first *Chemistry, General Chemistry* ('Kemija, Splošna kemija') in 1983, which was followed in the next year by *Chemistry, Inorganic Chemistry* ('Kemija, Anorganska kemija'). Later on, they published another textbook, the *»General and Inorganic Chemistry for Grammar Schools and Technical High-Schools« (Splošna in anorganska kemija za gimnazije, strokovne in tehniške šole)*. A revised edition of this book, *Chemistry for Grammar Schools 1* ('Kemija za gimnazije 1'), which was published in 2000, was co-authored by another of his colleagues, Prof. Nataša Bukovec.

In the first years of his independent career, his research efforts remained focused on the synthesis and structural properties of dimolybdenum(II) compounds with quadruple metal–metal bonds. Jurij and Primož Šegedin, at that time his Ph.D. student, managed to prepare a series of derivatives of the octahalodimolybdate(II) ions. The initial goal to find a link between the nature of the countercation and the stoichiometry of the halodimolybdate(II) ion led to the discovery of two isomeric forms of the diaqua-substituted ion, $[Mo_2Br_6(H_2O)_2]^{2-}$, whose unambiguous characterization relied heavily on the X-ray structure analysis. Already during his stay in the group of Prof. F. A. Cotton, Jurij realized the importance of the X-ray structure analysis on single-crystals in the characterization of compounds. All it took to know the real nature of the compound was a single well-diffracting crystal and of course, a diffractometer. We must not forget that in 1969 there was no such instrument in Slovenia or in Yugoslavia. With the availability of the first X-ray diffractometer for single-crystals in Ljubljana in 1974, the research options expanded enormously. That was also the beginning of a life-long collaboration and friendship with the first Slovenian crystallographer, Prof. Ljubo Golič, and his successor, Prof. Ivan Leban. Their fruitful scientific collaboration resulted, among other, in the characterization of pyridine, 2,2'-bipyridine and 1,10-phenanthroline derivatives of octahalodimolybdate(II) ions. The X-ray structures of two neutral species, $[Mo_2Cl_4(pic)_4]$ and $[Mo_2Br_4(pic)_4]$ (pic denotes 4-methylpyridine), confirmed the initially assumed *trans* distribution of the ligands within the molybdenum(II) coordination sphere. The other part of his research presents a seminal work on the classic coordination compounds of tungsten(III), whose chemistry was and continues to remain highly elusive. Jurij and Boris Čeh, at that time his Ph. D. student, managed to reduce a starting tungsten(IV) material $[WX_4L_2]$ (X = chloride, bromide and L = an aromatic nitrogen base). The new tungsten compounds found their place within a larger group, a series of analogous coordination species of chromium(III), molybdenum(III) and tungsten(III), with the compositions $[MX_3L_3]$, $[MX_4L_2]^-$, $[MX_5L]^{2-}$ and $[MX_6]^{3-}$, whose preparations and structural characterization represented a systematic and a comparative study both of their similarities and differences. The analogues were found to display very similar structures, some pairs could even be isotypic, and at the same time markedly different patterns of reactivity. The latter had a crucial impact over the synthetic methods employed for their preparation. One member of the series, *i.e.,* the $[MoCl_4(py)_2]^-$ (py = pyridine) ion, was shown to exist in two isomeric forms, with a *cis* or a *trans* distribution of ligands. Furthermore, a meticulous study revealed that the pyridinium salt of the *trans* isomer only exists in two polymorphic forms, with the main difference between the pair being in the relative orientation of the aromatic ligands. One form featured a *staggered* orientation of pyridine ligands, whereas the other an *eclipsed* one. The concomitant formation of the two polymorphs was rather intriguing. The explanation was provided by the theoretical calculations, which showed only a negligible energy difference between the two rotameric forms. Jurij and his group also defined reaction conditions for the controlled substitution of the halides with pyridine in the $[MoX_6]^{3-}$ ion. The step-wise substitution could be stopped at a highly reactive mono-substituted $[MoX_5(py)]^{2-}$ ion or left to proceed to di-substituted ions. The last decade of his research was dedicated to the coordination chemistry of molybdenum and tungsten in higher oxidation states. The chemistry of molybdenum(V) turned out to be extremely rich, as shown by the isolation of a variety of novel compounds containing a dinuclear $\{Mo_2(\mu_2\text{–}O)_2O_2\}^{2+}$ structural unit with metal ions linked *via* a single metal–metal bond. The $\{Mo_2(\mu_2\text{–}O)_2O_2\}^{2+}$ –containing compounds not only displayed interesting structures, but also served as models for theoretical calculations and studies of magnetism. A striking contrast to molybdenum chemistry was that of tungsten. It was the kind of chemistry that he seemed to enjoy the most: challenging, unpredictable and, at first glance, impossible to control. He kept on repeating, almost on a daily basis, the synthesis of a certain tungsten(III) compound, *i.e.*, potassium eneachloroditungstate(III), whose published preparations in *Inorganic Syntheses* lacked reproducibility. He did not stop until, after numerous repetitions, he managed to define the reaction conditions and thereby opened an entry point into the coordination chemistry of tungsten. I could go on enumerating the scientific achievements that he and his group achieved. His legacy encompasses over 70 research papers, some of them published also in the best inorganic chemistry journals.

I had known Jurij for decades. By setting himself as an example, he taught me that working in a laboratory is hard work, which sometimes pays off and sometimes it doesn't. Jurij was a superlative chemist who never stopped marvelling at the mysterious ways of chemistry, yet he remained modest and grateful for being given the opportunity to solve the tiny pieces of this great mystery. I am glad to have known him and I shall miss his critical views and sense of humour.

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Graphical Contents