

OBITUARY

Boris Kamenar (1929 – 2012)



Professor Emeritus Boris Kamenar, a distinguished Croatian chemist and an internationally recognized scientist and eminent intellectual, suddenly passed away at Premantura on the Adriatic coast on July 12, 2012.

Boris Kamenar was born on February 20, 1929 in Sušak, present day Rijeka, where he attended primary and secondary school. He went on to study chemical technology at the University of Zagreb graduating in 1953 and began his professional career as an engineer at The Cranes Factory and Foundry, "Vulkan", in Rijeka (1953–1956) where he established the Laboratory for Chemical and Mechanical Investigations. In 1956 he joined the group of Professor Drago Grdenić at the Ruder Bošković Institute in Zagreb working on problems of silicon and boron chemistry under his supervision. In 1960 he wrote the thesis entitled "*A New Method for Obtaining Pure Silicon and Boron*" and obtained a PhD degree of the University of Zagreb. Soon afterwards, in 1962, he was appointed Assistant Professor and then in 1966 Associate Professor at the Faculty of Science, University of Zagreb. In 1972 Boris Kamenar obtained a permanent position as Full Professor which he kept until his retirement in 1999. In 2000 he was awarded the status of Professor Emeritus of the Univer-

sity of Zagreb. In 1991 he was elected a Member of the Croatian Academy of Science and Arts.

B. Kamenar did his postdoctoral research in 1964/1965 and had an opportunity to work in the research group of Professor Dorothy C. Hodgkin, later Nobel Prize winner, at the Chemical Crystallography Laboratory of Oxford University. In 1971/72 he returned to the same laboratory as a Visiting Fellow of All Souls College of Oxford University. He was appointed Visiting Professor three times at the Universities of New Zealand: in 1980 he spent six months at Auckland University, and again in 1989/90 and then one term in 1995/96 at the Massey University in Palmerston North.

Since 1962, when he obtained a position as assistant professor at the Faculty of Science of the University of Zagreb, Boris Kamenar has pursued his academic career. He served from 1965–1966 as head of the Chemistry Department of the Faculty of Science, from 1982–1984 as head of Laboratory of General and Inorganic Chemistry and as Vice Dean (1968–1970) and Dean (1977–1978) of the Faculty of Science.

Boris Kamenar's scientific interest was X-ray structural analysis of inorganic, coordination and organometallic compounds, as well as organic compounds of pharmacological importance. The results of his scientific research have been published in 160 scientific articles, 20 professional papers, reported at international conferences and congresses and also many of them found a place in textbooks and monographs. As an internationally renowned scientist, Boris Kamenar chaired or co-chaired a large number of national and international conferences, committees, symposia. He was initiator, principal investigator of national and international research projects.

His scientific investigations have begun with pioneering research in the development of new methods of semiconductor production. He developed a new method for obtaining pure silicon and boron which is described in his PhD Thesis. In 1964, he and Professor Drago Grdenić have patented the process of obtaining very pure silicon. These studies were significant for the development of semiconductor industry in Yugoslavia.

Boris Kamenar's first structural studies, in period of 1960–1965, were related to structures of tin(II), arsenic(III) and antimony(III) compounds to elucidate the stereochemical function of the unshared electron pair. Results of Kamenar's structural investigations confirmed that Sidgwick-Powell rule could be applied also to heavy atoms.

3954

Kamenar and Grdenić:

770. The Crystal Structure of Stannous Chloride Dihydrate.

By B. KAMENAR and D. GRDENIĆ.

The crystal structure of stannous chloride dihydrate has been determined by methods of X-ray analysis. It follows from interatomic distances that the compound is dichloro aquotin(II) hydrate, $\text{Sn}(\text{OH}_2\text{Cl}_2)_2\text{H}_2\text{O}$.

The molecules of aquo-complex and water of crystallization form alternate double layers parallel to the (100) plane and linked by hydrogen bonds. The aquo-complex is pyramidal, which shows that the non-bonding pair of electrons of the tin atom is stereochemically active; the bond angles are low, proving a strong "lone-pair-bond-pair repulsion".

The crystal structure of such a common and simple compound as stannous chloride dihydrate has been studied in order to determine the co-ordination of water molecules around the tin atom, a point not only of interest for the structural chemistry of tin(II) compounds, but also having a general significance for the stereochemistry of molecules or complexes with a lone pair of electrons on the central atom.¹

The molecule of anhydrous stannous chloride is bent, with a bond angle of about 95°, as determined by the electron diffraction of the vapour.² This angle is a result of the influence of the lone pair of the tin atom on the bonding pairs, giving a triangular arrangement of pairs of electrons according to Sidgwick and Powell's rule.³ Thus, there are two possibilities for dihydrated stannous chloride, as pointed out in our preliminary communication – one or both water molecules may be co-ordinated to the tin. In the former case the complex would have to be pyramidal as a result of the tetrahedral arrangement of one non-bonding and three bonding pairs of electrons. In the latter, a distorted pyramidal configuration, as in the SnO or TeCl_4 structure, would result into one non-bonding and four bonding pairs of electrons. The complex with one co-ordinated water molecule with 55% electrons in a tetrahedral hybridization was *a priori* more probable and has been shown to be correct by the present investigation.

EXPERIMENTAL

Crystallographic and X-Ray Data.—The crystals of stannous chloride dihydrate, prepared from a saturated aqueous solution, are monoclinic prisms elongated along the *c*-axis direction. The crystals were described and examined crystallographically by Marignac, who in the present paper all crystallographic data are referred to the axes chosen by this author. The unit cell as determined from oscillation photographs has the dimensions: $a = 9.38 \text{ \AA}$, $b = 7.22 \text{ \AA}$, $c = 9.92 \text{ \AA}$, $\beta = 114^\circ 58'$. The axial ratios $a:b:c = 1.299:1:1.949$ agree well with the values $a:b:c = 1.2888:1:1.2452$ (and $\beta = 114^\circ 58'$) given by Marignac. There are four formula units in the unit cell [calculated density (D_c) 2.707, measured density (D_m) 2.710; $M = 225.64$; $U = 53.3 \text{ \AA}^3$, $F(000) = 416$]. Nickel-filtered Cu-K radiation was used. Systematic extinctions were observed only for $h0l$ reflexions with h odd and for $h0l$ with l odd. The space group is, therefore, $P2_1/c$ (C_{2h}^5 , No. 14).

Intensity Measurements.—Specimens cylindrically ground along the *b*- and the *c*-axis with diameters 0.39 and 0.33 mm., respectively, were sealed in Lindemann glass capillaries to protect them from the atmospheric moisture. All possible $(h0l)$ and $(h\bar{0}l)$ reflexions were recorded on multiple-film Weissenberg photographs by means of a Nonius integrating camera. The relative intensities of the reflexions were determined from the optical densities which were measured in the centre of each spot by means of a microdensitometer and corrected by means of the characteristic curve of the film. The number of $h\bar{0}l$ and $h0l$ reflexions observed was 71 and 84 (out of 85 and 98 possible reflexions), respectively. The absorption correction

¹ Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339.² Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 406.³ Sidgwick and Powell, *Proc. Roy. Soc.*, 1940, **A**, **176**, 153.⁴ Grdenić and Kamenar, *Proc. Chem. Soc.*, 1960, **312**.⁵ Marignac, *Ann. Mines*, 1856, **9**, 5.

Figure 1. The first page of the article published in the *Journal of the Chemical Society* (September, 1961.), p 3954–3958.

During this period he solved a number of charge transfer complexes and in 1973 he and Professor K. Prout have published review article *Crystal Structures of Electron-Donor-Acceptor Complexes* in a book *Molecular Complexes*, edited by R. Foster. Boris Kamenar has been involved in the X-ray structure determination of a large number of mercury(I) and mercury(II) compounds and complexes of iron, nickel, copper, niobium and molybdenum. He and his co-worker Branko Kaitner have written a review article about iron complexes for a book *Structural Studies on Molecules of Biological Interest*, a Volume in Honour of Dorothy Hodgkin (Clarendon Press, Oxford 1981). Boris Kamenar has been primarily engaged in investigations of molybdenum complexes and polyoxomolybdates, which can serve as models for understanding the structure and function of enzymes and also as catalysts in a vast number of chem-

ical processes. He and his co-workers have solved a significant number of such structures containing molybdenum in different oxidation states and surrounded by different type of ligands, especially those containing nitrogen, sulfur and oxygen.

Professor Boris Kamenar was involved in investigations of biologically and pharmacologically important organic compounds and their structures. His first result in this area, published in 1965, was the molecular structure of Eschenmoser's "pseudo-corrin", a compound obtained from the final stage of Eschenmoser's synthesis of corrin. A very nice research in which he participated was the determination of the crystal structure of a class of new azalide macrocyclic antibiotics (azitromycin) (1987) and potential antihyperglycemics from the class of dioxepino-azirines. This research was the result of his long-term cooperation with the Research Institute of the PLIVA Pharmaceutical Company. He solved the crystal and molecular structure of histamine H₂-receptor antagonist Burimamid, a new type of drug. This investigation was performed in collaboration with Smith, Klein and French Laboratories Ltd.

Professor Boris Kamenar was a dedicated teacher of Inorganic Chemistry and Crystallography at all levels of study and acted as a mentor to about thirty MSc and PhD students. His broad knowledge inspired his students and co-workers. During all this time he was an active member of the society, participated in many public and professional activities. He served as President of the Croatian Chemical Society (1976–1980), President of the Union of Chemical Societies of Yugoslavia (1976–1980), Secretary of the Yugoslav Center for Crystallography (1966–1990), President of Croatian Crystallographic Community (1991–2005), Vice-president (1978–1981) and president of the European Crystallographic Committee (1981–1984). From 2000–2004 and from 2011–2012 he served as president of Board for international collaboration of Croatian Academy of Science and Arts. He was of HAZU representative on the Governing Board of the European Science Foundation. Since 2005 he was a member of World Academy of Arts and Sciences and since 2009 Macedonian Academy of Arts and Sciences.

Boris Kamenar received several awards for his scientific and teaching contributions. In 1970 he received the "Ruđer Bošković" Award, in 1980 The Award of Zagreb, in 2000 The State Award for Lifetime Achievement, 2002 Medal of Božo Težak and in 2005 the Medal of Chemistry Department.

All of those who knew Professor Boris Kamenar will remember him as a meritorious scientist and professional. His colleagues and co-workers will miss his strong and optimistic personality.

Professor Marina Cindrić