INTERVIEW OF KAZUO YAMASAKI
(Nagoya University)

Hitoshi Ohtaki

Kazuo Yamasaki was born on March 15 1911. He was educated at the Imperial University of Tokyo where he received Rigakushi (corresponding to B.A.) in 1933 and Rigakuhakushi (corresponding to Ph.D.) in 1941. At that time, the education system was the old one, different from the present system. He subsequently joined Nagoya University in 1941, one year before the establishment of the Department of Chemistry, Faculty of Science, and he spent his entire career there until 1974, when he retired having reached the age limit.

Yamasaki received the Imperial Award of the Japan Academy in 1960 for the study of the Mural Paintings of the Pagoda of the Daigoji temple in collaboration with art historians. He also received the Koyama Fujio Medal from the Japan Society for Oriental Ceramic Studies, and the Forbes Prize from the International Institute for Conservation of Historic and Artistic Works, London. He was elected Member of the Japan Academy in 1989.

Yamasaki has served on various committees of the Chemical Society of Japan, and has been active in the Commission on the Nomenclature of Inorganic Chemistry, IUPAC from 1959 to 1985.

He was Secretary-General of the 10th ICCC held in Japan in 1967, and is Honorary Chairman of the Organizing Committee of the 30th ICCC to be held in 1994 in Japan.

He has authored or co-authored five books, and some 80 research papers in coordination chemistry.

H.O. Let's go back to the beginning of your life and your initial interests in chemistry.

I was born in Nagoya in 1911 where my father was a member of the Nagoya branch of a cotton trading company; I lived there until 1913 when my father moved to Osaka where my parents lived for almost 30 years. I attended the primary school (1918–1923), secondary school (1923–1927) and high school (1927–1930) in Osaka. As my father was in the business of cotton trading, the names of places such as Dallas, Texas and Bombay, India were familiar to me. A friend of my father who returned from Dallas gave me a small box which contained test tubes and some chemicals for doing simple experiments for children. This initiated my interests in chemistry. It was when I was in the higher class of the primary school.

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In the Osaka High School the chemistry teacher was Tokuichi Tsumaki who had graduated from the University of Tokyo in 1922, and he gave a clear and attractive lecture. This made me choose chemistry as my major at university. Tsumaki, whose background was organic chemistry, later visited the laboratory of Paul Pfeiffer in Germany and studied the cobalt complexes of Schiff bases. After coming home, he found in 1938 the oxygen adducts of these complexes, which were studied further by the group of M. Calvin during the Second World War and the results were published after the war.

H.O. Tell me about the Department of Chemistry of the University of Tokyo when you entered there.

When I entered the University of Tokyo in 1930, the University was composed of seven faculties: law, literature, economy, science, engineering, agriculture, and medicine. The Department of Chemistry belonged to the Faculty of Science and that of Applied Chemistry to the Faculty of Engineering. I entered the Department of Chemistry. At that time, the educational system was different from the present one, and a university education lasted for three years. Now we call it the old system. Most of the lectures such as physical chemistry, organic chemistry, analytical chemistry and inorganic chemistry and their experimental courses were assigned to the first and second years. In the third year, students had to choose the laboratory where the experimental work for the thesis of bachelor's degree was to be done. I decided to enter the laboratory of inorganic chemistry, the professor of which was Yuji Shibata. Ryutaro Tsuchida, who later became professor of Osaka University, had been an assistant to Shibata, but he had moved to Tokyo Metropolitan High School one year earlier.

H.O. Please tell me about Prof. Yuji Shibata and the reason why you chose inorganic chemistry.

The name of Prof. Yuji Shibata was known to me before I entered the University of Tokyo through his book. At the end of the 1920s, The Iwanami Publishing Corporation, one of the leading publishers in the field of natural and humanistic sciences, published courses on physics and chemistry at university level, which consisted of various subjects such as rare earth elements, geochemistry, catalytic hydrogenation of organic compounds, etc. Each subject was described in about 100 pages. Among these subjects, *Metal Complex Salts* by Yuji Shibata was included. I read it when I was a student of the Osaka High School. This small book was very interesting and I was completely fascinated by Shibata's fine prose on the biography of Alfred Werner. Even now I can still recite it after 60 years. After entering the University of Tokyo, the lecture on inorganic chemistry by Prof. Shibata was much more interesting to me than any other lecture. No specific lecture on coordination

chemistry was given. It was included in the lecture on the inorganic chemistry of metals.

May I take several minutes here to tell you about the career of Prof. Yuji Shibata (1882–1980)? He was the second son of Shokei Shibata, an eminent pharmacologist who had studied organic chemistry in Berlin under August Wilhelm von Hofmann during the period 1870–1874. Yuji Shibata graduated from the Department of Chemistry, University of Tokyo in 1907, and went to Europe in 1910.

He stayed in Europe for three years, one each in Leipzig (under Arthur Hantzsch), Zurich (under Alfred Werner), and Paris (under Georges Urbain). In Leipzig (1910–1911), he studied the colour of cobalt salts in solution, in Zurich (1911–1912) resolution of an optically active cobalt complex, and in Paris he measured the absorption spectra of several cobalt complexes.

After coming home in 1913, one year before the outbreak of the First World War, he was appointed associate professor of his alma mater, and he engaged actively in spectrochemical studies of metal complexes. The absorption spectra of more than 120 complexes of cobalt, chromium, nickel and copper were measured, and the results were published in French during the period 1915–1920.

In 1920, Yuji Shibata and his elder brother Keita Shibata, who was the professor of phytochemistry at the University of Tokyo, discovered an interesting oxidation reaction of myricetin, a flavonol derivative, by cobalt complexes. Not only myricetin, but also polyphenols such as pyrogallol were catalytically oxidized by cobalt complexes such as $[CoCl(NH_3)_5]Cl_2$. When I entered the laboratory of inorganic chemistry, the oxidation reactions by cobalt complexes were actively studied by measuring oxygen absorption using Warburg manometers.

The first substrate studied by me was a photographic developer, metol (monomethyl-*p*-aminophenol sulphate). Then catalytic oxidation of pyrogallol by colloidal metals such as silver, platinum and gold was studied.

The results obtained by the Shibatas and their co-workers were published in 1936 in a book *Katalytische Wirkungen der Metallkomplexverbindungen*. In this book, parts of my experiments carried out in 1933–1935 are included. As this book was written in German and the Second World War broke out in 1939, it was not well cited in the overseas literature, especially that published in English.

In 1974, 40 years after the publication of this book, I found a US Patent requested by Eastman Kodak Co. on the use of a cobalt complex such as $[Co(NH_3)_6]Cl_3$ as an amplifier in the development of colour films. Although no reference is made to the work of Shibata, I suppose that the chemists in Eastman Kodak studied the papers of the Shibatas and their co-workers.

H.O. What did you do after graduating from the University?

After graduating from the Department of Chemistry in 1933, I took a post-graduate course for two years, and in 1935 I was appointed assistant to Prof. Yuji

Shibata. The studies on oxidation reactions continued, but the mechanism of the oxidation is difficult to elucidate by measuring the oxygen absorption only. As the reacting solution became black, no absorption spectrum measurement was possible. After having tried several oxidizable compounds such as cysteine without successful results, I decided finally to change the subject of my research, and proposed to Prof. Shibata a study of the absorption spectra of 2,2′-bipyridine complexes. The complexes of the type $M(bipy)_3$ were first reported by F. Blau in Germany in the last century, but no study of their colours was made.

In 1936, no 2,2′-bipyridine was commercially available in Japan and I tried to prepare it by heating pyridine with anhydrous iron(III) chloride in a small autoclave which the inorganic chemistry laboratory had. Anhydrous iron(III) chloride was also prepared in the laboratory by passing chlorine generated by the reaction of hydrochloric acid and potassium permanganate, over iron nails packed in a hard glass tube. The iron complex of 2,2′-bipyridine thus obtained was decomposed by alkali and the bipyridine was extracted by an organic solvent. The yield was small, only a few grams at a time. This was used to prepare iron complexes first. After analyzing the complexes and measuring the absorption spectra, the complexes used were decomposed and the bipyridine recovered was used again to prepare complexes of another metal. Thus $M(bipy)_3$-type complexes of iron(II), iron(III), cobalt(II), cobalt(III), nickel(II), copper(II), and zinc were prepared and their absorption spectra were measured. In addition to these complexes, several new complexes of iron and cobalt were prepared and their properties, including absorption spectra, were studied.

The measurement of the absorption spectra was not easy at that time. When Prof. Shibata returned from Europe in 1913, he was able to obtain a medium quartz spectrograph, Type E2 of Adam Hilger Co., London. Until around 1935, Shibata was the only specialist of spectrochemistry in Japan and he was asked by various researchers to measure absorption spectra. As the assistant of the inorganic chemistry laboratory I performed many measurements for substances provided by other workers, including biologists and medical researchers. The laboratory, however, was not well equipped. A Nutting spectrophotometer for the visible region and a quartz spectrograph for the ultraviolet region were all the spectroscopic instruments we had. No rotating sector was available, and we only performed semi-quantitative measurements of absorption spectra by the so-called Hartley–Baly method.

I therefore used Victor Henri's method to estimate the extinction coefficients of the metal complex solutions. The laboratory was in such an obsolete state. In 1941, I obtained Rigakuhakushi (corresponding to Ph.D.).

H.O. Please tell me about the establishment of Nagoya University.

Nagoya University started as a prefectural medical college in 1881, and it has a long history. The establishment of the 7th Imperial University in the central part of Japan after Tokyo, Kyoto, Tohoku (Sendai), Kyushu (Fukuoka), Hokkaido

(Sapporo), and Osaka had been desired for a long time. Finally, in 1939, the establishment of the Faculty of Science and Engineering was agreed, and Nagoya Medical College became the Faculty of Medicine of Nagoya Imperial University. Departments of Mathematics, Physics, Chemistry and Biology of the Faculty of Science, Nagoya Imperial University were to be started in the spring of 1942.

Professor Shibata, who retired by age limit from the University of Tokyo in 1942, was to be the Dean of the Faculty of Science in Nagoya. He recruited several young scientists as the members of Faculty of Science. I was asked if I would join the staff of the Department of Chemistry, and I accepted immediately. In April 1941, I was appointed assistant professor and began to prepare the establishment by going back and forth between Tokyo and Nagoya, but the task was a difficult one. The war between China and Japan had started in 1937 and import of back numbers of chemistry journals and books was not possible.

Fortunately, the back numbers of periodicals such as *Journal of the Chemical Society, Angewandte Chemie, Zeitschrift für Anorganische und Allgemeine Chemie,* and *Nippon Kagaku Kaishi* (*Journal of the Chemical Society of Japan*) were obtained in Japan. The Department of Chemistry of the University of Tokyo lent us duplicate volumes of *Berichte der Deutschen Chemischen Gesellschaft.* I still remember the purchase of *Chemical Abstracts,* Vols. 1(1907)–33(1939) in Tokyo at the price of ¥4600, which corresponds to about $40,000 today. We borrowed platinum crucibles for the student experiments in analytical chemistry from the University of Tokyo because platinum was recovered by the government to make platinum electrodes for electrolytic production of concentrated hydrogen peroxide used for rocket fuel.

H.O. What happened to Nagoya University during the Second World War?

By the outbreak of the war in December 1941, the arrival of current numbers of chemistry journals had completely stopped, but during 1942 and 1943 there was no great problem in the University and the education of the first year students started in the spring of 1942 in wooden buildings built in the eastern part of Nagoya. In 1944, air raids on Nagoya began and in March 1945 severe bombardment destroyed most parts of the city of Nagoya, and the Department of Biology building was burnt down, but the Department of Chemistry survived. Staff members and students were evacuated to the inner part of Central Japan.

After the end of the War, the education in the University started again in November 1945. Fortunately, electricity, city gas and well water were available in the University and we somehow managed to continue student experiments. The difficult conditions of general life continued until about 1949.

H.O. Now let us move on to the research done after the war.

Well, many things happened after the war. Professor Shibata retired as the Dean in 1949 and one year later he was appointed the President of Tokyo

Metropolitan University. The educational system was changed and in the new system a university education required four years.

As for research, in the inorganic chemistry laboratory the measurement of absorption spectra became easy by the introduction of a Beckman-type spectrophotometer. After doing several studies in the field of stability measurements of complexes in solution, and synthetic studies of several rhodium complexes, studies on optically active complexes which I had been planning for a long time started in 1967 when an instrument for measuring optical rotatory dispersion and circular dichroism spectra became available.

First we tried to improve the preferential adsorption method for resolution of complexes, which had been devised by R. Tsuchida in 1935 by using dextro- and laevo-rotatory quartz crystals. Yuzo Yoshikawa, one of my co-workers, who is now Professor of Inorganic Chemistry at Okayama University, used an ion-exchange cellulose as the adsorbent in the column chromatography to resolve $[Co(en)_3]Cl_3$. When eluted by 0.1 M HCl, resolution of only 7% was observed for the first effluent. I suggested the use of sodium (+)-tartrate solution as the eluting agent, and a resolution percentage of 80% was then observed. After several attempts at ion-exchange, Sephadex was adopted as the adsorbent and total resolution was achieved.

This method is not only effective for the complete resolution and preparative separation of optical isomers, but is also effective for the separation of geometrical isomers. We have applied it to complexes with various polydentate ligands with successful results. The absolute configurations of optically active complexes thus obtained were determined using X-rays by Yoshihiko Saito and his co-workers in Tokyo. This chromatographic resolution method is now widely used in various laboratories. A review was published by us in *Coordination Chemistry Reviews* in 1979.

H.O. Please tell me about your work in fields other than coordination chemistry.

In 1939, I began to study the pigments used in the 8th-century wall paintings of the Horyuji temple in Nara. This was a part of the government repair project for the temple, which lasted until 1954. Professor Shibata was a member of the Repair Committee for the first several years. The work was an application of emission spectrography, because the pigment samples obtained were very small. It was interesting to me, and I visited the Horyuji temple many times even during the war and became acquainted with art historians, archaeologists and artists who were copying the wall paintings. This work was later extended to the chemical studies of ancient Chinese and Japanese bronzes, glasses, and potteries and porcelains, and so-called archaeological chemistry became one of my life-long works. Now, conservation science is a very important field and national conservation laboratories for cultural property were established in Tokyo and Nara.

Another work is the translation into Japanese of the *Nomenclature of Inorganic Chemistry*, IUPAC. From 1959 until 1985 I participated in the Commission on

Nomenclature of Inorganic Chemistry in various capacities, first as guest, then associate member and finally as national representative. The Japanese translation of the 1961 and 1971 editions of the so-called Red Book (*Nomenclature of Inorganic Chemistry*) were published. The translation of the third edition will be published at the beginning of 1993, and this will conclude my activity in this field. Nomenclature is very important, but a difficult and tedious work, and very few people understand its importance.