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INTERVIEW OF HAYAMI YONEDA
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Hayami Yoneda was born in Kashiwara, Osaka Prefecture in 1923. He graduated from the Department of Chemistry, Faculty of Science, Imperial University of Osaka in 1945. After graduating from the university, he remained there as a Special Graduate Student under the supervision of Prof. R. Tsuchida for five years. In 1950, he became a lecturer at Wakayama University where he worked for 22 years as assistant professor and professor until he moved to Hiroshima University in 1972. He received Doctor of Science degree from Osaka University in 1957.

In 1961, he went to Florida State University and worked in the laboratory of Prof. G.R. Choppin as a research associate for two years. He was invited to the Technical University of Denmark as a visiting professor in 1970–1971. In 1972, he was nominated for professor of coordination chemistry of Hiroshima University and worked there for 15 years until he retired in 1987, when became a Professor Emeritus Hiroshima University. After his retirement from Hiroshima University, he joined the faculty of Okayama University of Science and is now a professor there. During his Hiroshima days, he served as an executive for the Chemical Society of Japan in 1977–1978, and was the head of the Chugoku-Shikoku Branch of C.S.J. in 1986.

He has shown his excellent chemical sense in pioneering works in three important aspects of coordination chemistry, i.e. the introduction of NMR technique to coordination chemistry, ingenious interpretation of the chomatography of metal complexes, and the elucidation of the chiral discrimination mechanism in metal complexes.

K.M. First of all, I would like to know what prompted you to major in chemistry.

Before talking about that, I want to mention my personal history briefly. I was born in 1923 at Kashiwara-cho in the suburbs of Osaka. My father was an acupuncturist and my mother a midwife. They also had two daughters, one older and the other younger than I, but both died when I was young. So, I was the only child remaining. We had no scholars or well-educated people among our relatives; there was no academic atmosphere around me. After graduating from a local primary school, I went up to the Tennoji Middle School in Osaka and then to the Osaka High School. A Nobel prize laureate, Ken-ichi Fukui, graduated from this high

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school. The high school before the Second World War was a preparatory school to seven Imperial Universities and so the entrance examination was rather severe. I fortunately passed it to take a science course. To my disappointment, all my middle-school teachers said that they thought I took a course for literature when I informed them of my success in the examination.

My father died in 1940 when I was a second year student. In December of that year, Japan started the war against the allied forces of USA and UK, but a free and academic atmosphere still remained in the high school. In those days, there was a rumour that Prof. Hideki Yukawa had published an epoch-making paper in the field of theoretical physics and he would surely get a Nobel prize. Stimulated by the rumour, many students wished to major in physics at university. My mother wanted me to become a medical doctor, but I had no inclination for medical science because the biology I learned at the high school had not yet been well developed, particularly in logic and so I supposed that a medical course would force us to memorize as many things as possible without clear interpretations. I wanted to be involved in pure science. I was also one of the students influenced by Prof. Yukawa. However, I had no confidence in my ability to study physics so I eventually chose chemistry as a major at Osaka Imperial University by a process of elimination.

K.M. *What was your motive for researching in coordination chemistry?*

I was deeply impressed and attracted by the vivid and clear lectures given by Prof. Ryutaro Tsuchida at Osaka Imperial University. He willingly accepted me in his laboratory. He had already made many significant contributions to inorganic chemistry with his keen intuition and unique ideas. Notable ones were systematic studies on the absorption spectra of metal complexes, asymmetric adsorption of metal complexes on quartz, measurements of absorption spectra of fine crystals with a spectrograph combined with a microscope, and the coordination theory of valency. Here, I want to mention the last one, which has been unfairly neglected abroad. Professor Tsuchida proposed his coordination theory of valency in which bonding pairs of electrons and non-bonding (lone-pair) electrons are treated equivalently in space and are located symmetrically around the central atom to determine the structure of the molecule or polyatomic ion (R. Tsuchida, Bull. Chem. Soc. Jpn., 14 (1939) 101). His idea was basically the same as the valence-shell electron-pair repulsion (VSEPR) theory proposed by Sidgwick and Powell in 1940 and later refined by Gillespie and Nyholm in 1957. Professor Tsuchida sent his reprints to some American and European scholars, including Sidgwick, but he got no response. On the contrary, Sidgwick and Powell in the following year, published their paper containing the same idea. It was on the structure of a square planar complex $[ICl_4]$ ion in which they proposed that two lone-pairs occupy the axial positions and four pairs of bonding electrons reside on the square plane. Professor Tsuchida felt very chagrined at their paper because it did not refer at all to his earlier paper mentioned above.

The concept of the spectrochemical series, on the other hand, has fortunately been accepted throughout the world as having been founded by him.

K.M. After graduating from the university, you remained in Prof. Tsuchida's laboratory for a while. Please talk about your research in those days.

To be honest, I don't want to, because those days were the most miserable in my research life. When I look back at those days I remember almost nothing worth noting about research. It was Prof. Tsuchida's principle that each student should decide his own research target by himself. I always felt frustrated because I could not find any nice target suitable for me.

In 1961, I joined with Prof. Gregory R. Choppin as a post-doctoral fellow at Florida State University. I was engaged there in measuring stability constants of rare earth complexes, but I was still wondering what I should research on, and how I could utilize my talents, if any, for research.

K.M. How did you finally find research subjects which suited and pleased you?

On reflection, I was a theory monger who does not fall under the category of theorist, a theory monger who judges everything as hard as possible within the range of his common sense. This is one of the reasons I was so deeply impressed by Prof. Tsuchida. It was the study of paper chromatography that can be ranked as the first step to research work fitting my character. After I moved to Wakayama, I was still attending a colloquium held every week at Prof. Tsuchida's laboratory where I came across an interesting paper. It reported that R_f values obtained by paper chromatography for a series of nitroamminecobalt complexes increase with the number of nitro groups present. It reported the result only; no interpretation was presented. A bright idea occurred to me. I could see differently charged complex ions flowing on a negatively charged surface of filter paper, at different rates depending on the strength of their electrostatic attraction and/or repulsion. I lost no time in examining R_f values for more than 20 cobalt(III) complexes and obtained results perfectly consistent with my interpretation. Through this work, I could at last find my way of research and I was somewhat confident of my intuition. With this work as a turning point, I started NMR studies and chromatographic studies of metal complexes.

In the early 1960s, there had appeared only few examples of NMR spectra of cobalt(III) amine complexes, because they are readily subjected to proton exchange in aqueous solution. The spectra were recorded in D_2O solution acidified to depress the proton exchange. I thought simply that the complexes should be dissolved in neat acid. Since we had no NMR in Wakayama University, I asked Yukiyoshi Morimoto, one of my early students working at the laboratory of Fujisawa Pharmaceutical Co., to measure NMR spectra of some diamine and pentaammine cobalt(III) complexes in trifluoroacetic acid. As I expected, stable and reproducible spectra were obtained, but they were all composed of broad peaks, looking like IR spectra. The NH_2 signals of tris(en) and tris(pn) complexes appeared as a very broad quartet. I intuitively speculated from the appearance of the signal that the ligand motion was suppressed under the influence of the central metal; if the temperature is raised sufficiently, en and pn should start to rock and the AB pattern finally coalesce to a singlet (I noticed later that this speculation was theoretically wrong). I wanted to check my speculation, and so wrote a letter to Gregory, with whom I had worked earlier at FSU, asking him to arrange for me to measure the temperature dependence of the NMR during summer vacation. I left Japan for USA in July 1966, assuming that I could get the expected results and go directly to Switzerland to present them at the ICCC to be held at St. Moritz. I had no travel fund and so I had to borrow my salary in advance. The rest of my family was forced to have frugal meals for a while.

At FSU, I found that the broad quartet due to the NH_2 protons coalesced to a broad singlet upon increasing the temperature. The CH_3 signal of the free pn appears as a doublet, but it becomes a broad singlet in the tris(pn)cobalt(III) complex. This broad singlet also became a doublet upon increasing the temperature. These observations were taken as evidence for the ligand motion taking place at elevated temperatures. I presented these results at St. Moritz. Professor J.C. Bailar praised my work highly. I also became acquainted with Prof. Flemming Woldbye from Denmark at the conference who brought me good luck afterwards.

I planned to attain optical resolution of the tris(en)cobalt(III) complex by electrophoresis, using varying concentrations of aqueous sodium *d*-tartrate as a supporting electrolyte, but in vain. I interpreted this as follows; since only the Λ enantiomer of the complex selectively separates from the saturated solution of the *d*-tartrate salt, it is evident that chiral discrimination is also attained in the saturated solution. Then, if electrophoresis is carried out under conditions similar to the saturated solution, optical resolution should be attained. I imagined that $[Co(en)_3]^{3+}$ would feel as if it were in the saturated solution, when it is surrounded by many Al^{3+} ions in the supporting electrolyte solution. As expected, optical resolution was achieved only when Al^{3+} ion was added in excess. I showed this result to Flemming who was visiting Japan by chance. He was interested in it and later invited me to Denmark as a visiting professor. In Denmark, however, I found my idea completely wrong; it was not the *d*-tartrate ion but a polynuclear complex anion comprised of some Al^{3+} and *d*-tartrate ions that was responsible for optical resolution of $[Co(en)_3]^{3+}$. In this way, my thinking is so intuitive that I often speculate incorrectly. But I was often lucky to arrive at the desired result.

K.M. Please tell me about your academic situation when you moved to Hiroshima University and organized your research group?

I was appointed a professor of coordination chemistry, newly established at Hiroshima University, in 1972, one year after I had returned from Denmark. I organized my own research group, called "koza", which usually consists of one professor, one assistant professor and two research associates as staff. I took Dr. Yoshihiko Kushi (crystal structure analysis) from Osaka City University, Dr. Ushio Sakaguchi (magnetic resonance) from the University of Tokyo, and Dr. Katsuhiko Miyoshi (solution chemistry) from Hiroshima University. Usually, "koza" was often organized with staff from the same laboratory of the same university, and so it had usually a familial atmosphere. By contrast, my "koza" was a jumbled group similar to an American research group. This is, I think, one of the reasons we could keep the high level of research activity for a long time.

K.M. I think your main research work at Hiroshima University involved studies on the mechanism of chiral discrimination of metal complexes. I would like you to give a survey of them and to evaluate them yourself.

I adopted a strategy to find firstly a one-to-one contact mode between complex ions to be resolved and resolving agents by means of X-ray crystal structure analyses and then to elucidate the mechanism of chiral discrimination, assuming that similar one-to-one contact modes are retained in solution. This strategy might seem to be too optimistic, but it brought me a successful result for the $[Co(en)_3]^{3+}$–*d*-tartrate system. We could establish the mechanism of chiral discrimination of $[Co(en)_3]^{3+}$ and related complexes by *d*-tartrate. Being encouraged by this good luck, we could also establish the ion association modes responsible for the chiral discrimination of these complexes with antimonyl *d*-tartrate with the aid of the systematic analysis of the CD spectra and chromatographic behaviour of these complexes. I feel happy to have had clear images for chiral discrimination by *d*-tartrate and antimonyl *d*-tartrate ions in solution. I appreciate highly the contributions to this problem by Ushio and Katsuhiko. I am satisfied especially with a series of works you (Katsuhiko) have done. You established that ion association with these resolving agents takes place concomitantly along different directions of the complex (e.g. the C_2 or C_3 axis) and that one particular association mode along a particular direction predominates over the other modes to attain chiral discrimination in practice.

On the other hand, chiral discrimination in a crystal is effected through a variety of group-to-group interactions between complex ions and resolving ions. It cannot be ascribed simply to a particular interaction. To make the matter worse, even if the crystal structure has been completely determined, special insight is necessary to extract meaningful characteristics of the packing mode of composite ions. Moreover, even if the packing pattern is looked upon, for example, as a collection of chains or a pile of layers composed of cations and anions concerned, it is still difficult, from mere comparison between the crystal structures of a diastereomeric salt pair, to guess which is more soluble or less soluble, because quite reasonable packing modes are always found in both crystals. Under these circumstances, we could actually publish only a small number of papers from our extensive structural data. I highly appreciate some work done by my graduate students among these papers. Notable ones are on the spontaneous resolution of $K_3[Co(ox)_3]$ by Hiroshi Okazaki and on structural analyses of racemic tartrate and two *d*-tartrate salts of $[Co(en)_3]^{3+}$ by Tsutomu Mizuta. I want to express my deep thanks to Yoshihiko, assistant professor at that time and now a professor at Osaka University, who guided these talented students to successful results.

K.M. To conclude this interview, I would like to ask you who had the greatest influence on your way of thinking throughout your life.

Professor Tsuchida did, of course. No one has been more influential than he in my way of thinking and my way of research as well as my way of life. I have seen a number of amazingly talented scholars, but they are, after all, persons unrelated to me. Naturally, I respect them highly but they have exerted no significant impact on my way of thinking.