INTERVIEW OF HIDEO YAMATERA
(Daido Institute of Technology)

J. Fujita

Hideo Yamatera was born in Kyoto on January 1st 1924. He was educated at the University of Tokyo for eight years, three years as undergraduate and five as graduate student. In 1951, he was appointed as a lecturer at Osaka City University. In 1958, he moved to Rikkyo University in Tokyo, and in 1967, he joined Nagoya University where he served 20 years as a professor. He is now a professor at Daido Institute of Technology in Nagoya. In 1982, he received the Award of the Chemical Society of Japan for the origination of the Yamatera rule in the absorption spectra of metal complexes. This rule is practically an application of the angular overlap model but preceded it by seven years. In addition to this work, he has published many papers devoted to various fields of coordination chemistry as well as solution chemistry and radiochemistry.

J.F. Before asking you about your academic history, tell us how you became interested in chemistry?

In my boyhood, I liked to grow vegetables and flowers. I was delighted to see that vinegar and soap solutions changed the colour of the flowers of morning glory. I also made rubber-band driven boats and planes and a simple electric motor. Arithmetic was my favourite subject and I liked to solve numerical and geometrical puzzles. My father generously bought for me books in which I showed interest. Among the books were a four-volume handbook of physical and inorganic chemistry and a few books on mathematics. When I was to take an entrance examination of a university, I chose chemistry because I knew that I liked practical science rather than abstract science. (The late) Professor M. Kawai's lecture of chemistry at Eighth Higher School (a school of the pre-war educational system which gave a three-year preparatory education to candidates for university students) may have oriented me to chemistry. He gave lectures based on a German text book he had recently bought. He was earnest but clumsy in lecturing and sometimes stopped lecturing for a while to think about the matter under consideration. Such breaks gave me opportunities of thinking about the subject and may have had a good educational effect.

J.F. You graduated from the University of Tokyo in September 1945, immediately after Japan surrendered to the Allied Forces. Could you tell us something about

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laboratory circumstances in those days? Who was your professor at the University of Tokyo? And what was the first subject of your research?

In 1945, Tokyo was under frequent bombardment by the American Air Force. Professors of the University of Tokyo kindly secured small temporary laboratories scattered outside Tokyo, where their students could safely do their experimental work. The subject (the late) Prof. Kenjiro Kimura assigned to me was the extraction of rare alkalis from the brine of the Arima hot spring, a spring famous for its high sodium chloride content and high radioactivity. My workroom was near the site of the hot spring, in a valley at the back of Kobe. Assistant Professor Kazuo Kuroda (P.K. Kuroda, who later became Professor at the University of Arkansas) was my supervisor. Professor Kimura occasionally visited Arima, travelling many hundreds of kilometers from Tokyo. At Arima, people evaporated the brine to separate sodium chloride and to obtain lithium chloride from the residual liquid. I used the solution which was left after the precipitation of lithium carbonate to extract rubidium and caesium chlorides. My workroom had been used as an office and was poorly equipped. To obtain pure hydrochloric acid, for example, industrial acid was heated with a charcoal burner and the vapour was liquefied with wet-towel cooling using a long glass tube loosely connected to a retort without a ground joint. There was no ventilation, so that the laboratory was fogged by hydrochloric acid mist. I obtained several tens of grams of raw $Cs_3Sb_2Cl_9$ there. Further purification and conversion to the chloride had to be done in a laboratory with better conditions. So I went to Tokyo, where I survived a bombing. The university laboratory also escaped the bombardment and pure caesium chloride was obtained. The major part of the product was sent to a factory for photoelectric tubes to be made, but it disappeared in the bombardments before the tubes were made. A minor part of the product was used for the search of element 87 with X-rays. We did not know the discovery of francium due to lack of information during the war. Kuroda and I found a barely observable line at the site of $L_{\alpha 1}$ of element 87. However, our claim was not endorsed by Kimura. He had practised X-ray spectroscopy at the Bohr Institute under Prof. Hevesy. His sharp eyes perceived the faint line not to be an L. By referring to a table, I found that a pair of brômine K_α lines would appear around the 87 $L_{\alpha 1}$ site.

J.F. You started to do research with inorganic analytical chemistry. When and how did you become interested in coordination chemistry, in particular colour, namely the electronic spectra of metal complexes?

When I aimed at entering the University of Tokyo as a chemistry major, inorganic qualitative analysis was among the subjects of the entrance examination. So I earnestly practised the analysis. In the course of this, I became very interested in the reactions of ions, especially those accompanied by colour changes. In 1950, the first post-war Symposium on Coordination Chemistry of Japan was held at the Tokyo Institute of Technology. I attended the symposium and was attracted to coordination chemistry. The next symposium was organized by (the late) Prof. Ryutaro Tsuchida in Osaka in 1952, when I was working at Osaka City University. At this symposium, I read a paper on the preparation of a new compound $Cs_3Fe_2Cl_9$. This was a result of a study of the triple chloride of caesium, antimony(III), and iron(III). Because the iron content of this compound was variable, I thought that the compound might be formulated as $Cs_3(Sb,Fe)_2Cl_9$. I tried to prepare an iron compound isomorphous to $Cs_3Sb_2Cl_9$ and I obtained it. When hydrochloric acid solutions containing caesium, antimony(III), and iron(III) were left many weeks on a shelf, crystals ranging from dark purple to yellow in colour separated out. The colours of the crystals, which were later confirmed to be a series of mixed complex salts $Cs_4[(Sb^{III}, Fe^{III})Cl_6][Sb^{V}Cl_6]$, aroused my interest and led me to the study of the spectra of metal complexes. My interest in cobalt complexes originated from my educational activity at Osaka City University. I prepared many cobalt(III) complexes to select several that would be appropriate for the training of students in preparative chemistry.

J.F. One of the marked contributions you made was the introduction of the Yamatera rule, that is your version of the "angular overlap model", to ligand field theory in the middle of the 1950s when you were working at Osaka City University. Could you tell us the story or background behind the thinking of this model?

When I was interested in the colour of metal complexes, I fortunately had Prof. Tsuchida's book *Colour and Structure of Metal Compounds* (in Japanese). I read this book with great interest, but was not entirely satisfied with his theory. The crystal field theory did not satisfy me because, by experience, I knew that the coordinate bonds are not simply electrostatic. Another motivation for a theoretical study was that I, together with the members of the laboratory, had read Eyring–Walter–Kimball's *Quantum Chemistry*. I owe much to them, especially to the youngest and most active member, Dr. Seiichi Kanda, now Professor of Tokushima University, and the next youngest, Dr. Masayasu Mori, recently retired from professorship at Osaka City University. I first followed Mulliken and his group in estimating orbital energies, but the results of my calculations were far from the observed values. Then I reluctantly followed the semi-empirical method of Wolfsberg and Helmholz to interpret the spectrum of the hexaamminecobalt(III) ion. When I completed this work and told friends about the results, I was informed that the famous 1954 papers of Tanabe and Sugano had just been published and Yoko Kuroda and Kazuo Ito were going to publish their results on the LCAO treatments of metal complexes. I then changed the targets of my research to more inorganic issues in which empirical parameters were available. As an inorganic chemist, I had a lot of information about the absorption spectra of complexes related to each other, thanks to Tsuchida's group and Linhard and Weigel. Their results showed that the spectra resembled each other. So I applied a perturbation method based on the LCAO theory in order to explain the spectra of the complexes related to the hexaamminecobalt(III) ion by ligand substitution. The rule I found for the shift of the absorption bands associated by ligand substitution was further tested by (the late) Prof. Yoichi Shimura and his group, and was named the Yamatera rule by him.

J.F. In 1965, C.K. Jørgensen and C.E. Schäffer proposed the angular overlap model. In my understanding, the basic idea of the model is essentially the same as yours, although the model is formulated in a more generalized form. Did you have any contact with them during those days? When did you meet them for the first time?

I owe much to Prof. Jannik Bjerrum and his students since 1956, when a list of publications from his department was received by Osaka City University and on request I was given about 30 reprints, including Professor Jørgensen's. Although the papers were based on the crystal field theory at that time, they stimulated me very much. I had communication with Jørgensen and received many reprints from him. In 1963, when I was working with Prof. Gilbert Gordon as a research associate at the University of Maryland, Jørgensen visited American Cyanamid Co. at Stamford, Connecticut. He asked me to come to Stamford to see him and kindly asked me to join his group at Cyanamid European Research Institute in Geneva. I was delighted to accept the offer, but eventually I could not go to Geneva because I was finishing a two year's leave from Rikkyo University and was not granted another year. If I could have worked in Geneva at that time, I would have had a wonderful opportunity of cooperating with Jørgensen and Schäffer in formulating the angular overlap model. It was 1973 when I first met Prof. Schäffer at the XVth ICCC in Moscow. At the XIIth ICCC in Sydney 1969, Schäffer kindly cited my 1957 and 1958 papers in his plenary lecture as the first proposal of the angular overlap model, although the application was limited to six coordinated orthoaxial chromophores. Schäffer and Jørgensen considered the effect of the ligand on the orbital energy of the central ion as perturbation, while I treated the ligand substitution, that is the difference between the effect of the ammine ligand and that of another substituent, as perturbation. Their angular overlap model was formulated independently of mine and later they found that my model was, in effect, the same as theirs when their general model was applied specifically to octahedral complexes.

J.F. Since then, how have you been cooperating with the Copenhagen group?

Professor Schäffer first visited Japan in 1974 on a JSPS (Japan Society for the Promotion of Science) program, and I visited Copenhagen in 1977 and again, by invitation, in 1983. An academic exchange agreement was made between the University of Copenhagen and Nagoya University in 1984. Since then we have met each other almost every year. We always discuss matters very frankly and sometimes we differ in opinion. Schäffer's criticisms have always been very useful for me to modify arguments to remove self-complacency and to avoid misunderstanding. Since

1985, we have cooperated in the study of the ligand field of conjugated bidentate ligands by the angular overlap model. The cooperation has been continued in spite of my retirement from Nagoya University. Daido Institute of Technology also made an agreement with the University of Copenhagen to support the cooperation. Some of the results of this collaboration were published in *Inorganic Chemistry* in 1991. You (Fujita) also published a few joint papers with Frode Galsbøl and his students. I am very happy that the cooperation with Schäffer and his group has been developed by you to include exchanges of students and that the exchange between the universities has been extended to disciplines other than natural science.

J.F. In addition to the angular overlap model studies, what other subjects have you been interested in?

Since I joined Nagoya University I have been interested in the chemistry of electrolyte solutions, especially in ion–ion and ion–solvent interactions as important factors of reactions of metal complexes in solution. My students treated these subjects from various points of view: electrostatic (in sulphates of bivalent metals), hydrogen bonding (in tris(ethylenediamine)cobalt(III) salts), and hydrophobic (in cation–cation association of tris(phenanthroline)ruthenium(II) ions and in association of surfactant ions), and also static or equilibrium and dynamic or time-correlated points of view. Yuichi Masuda, who is now an assistant professor at Ochanomizu University, applied the NMR relaxation technique to investigate interactions in solution. For this purpose, complex ions were especially useful because they can be made to contain desired nuclei and to have desired properties: physical properties such as size, shape, and charge, and chemical properties such as firm or loose hydration, hydrogen bond formation, and hydrophobic properties. Recently, I have been interested in interpreting the shapes of inorganic molecules and complexes in terms of an extended angular overlap model.

J.F. I would like to ask you about education at universities. Was it helpful for your research or not?

Devotion to education often provided me with a clue to a new development in research. Because I did not consider coordinate bonds as electrostatic, I was not much interested in Basolo's crystal field activation energy. When I was to give a lecture on advanced coordination chemistry, I thought I should, for fairness, teach Basolo's theory. While I was carefully following his theory, an idea came to me that a similar theory could be formulated with the angular overlap model. I was then able to propose ligand field activation energy on the ground that coordinate bonds are covalent to an appreciable extent. This idea of ligand field activation energy better explained the observed relative rates of ligand substitution. Preparation of cobalt complexes for educational purposes, as I said before, is another example. My understanding of the general properties of cobalt complexes was established through this series of experiments. Education was not only for students, but also for myself. Through education of the students, I could pick up pieces of basic and important ideas that would otherwise escape my attention.

J.F. Coordination chemistry has changed a great deal since you started to work. Could you tell us something about your views on the present situation of coordination chemistry in Japan?

When I started my research in coordination chemistry, only three professors in Japan had an active group of coordination chemists: Taku Uemura of the Tokyo Institute of Technology, Ryutaro Tsuchida of Osaka University, and Kazuo Yamasaki of Nagoya University. Professor Kimura, who was an analytical, radio- and geochemist, was generous to his students in their selection of subjects so that some of his students became coordination chemists, for example Kazuo Saito and myself. The total number of active Japanese coordination chemists in 1950 was about 30, including small groups and independents. The number of active coordination chemists in Japan has increased by more than ten times in about 40 years. Novel compounds have been prepared and new methods have been introduced. It was Prof. Tsuchida's opinion that every inorganic system can be considered as a complex. Coordination chemistry is now related to all fields of chemistry and even to physics, biology, and geology. I do hope that young coordination chemists will make contributions not only to traditional coordination chemistry but also to other fields of science and technology.