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INTERVIEW OF SHOICHIRO YAMADA

Sigeo Kida

Shoichiro Yamada was born in Sakai, Osaka, Japan in 1922. He majored in chemistry in the Department of Chemistry, Faculty of Science, Osaka University and received his B.Sc. and Dr.Sc. under the guidance of Professor R. Tsuchida. He joined the faculty at Osaka University in 1945, becoming a Professor of Chemistry in 1964, where he remained until his retirement in 1986. He is now a Professor Emeritus of Osaka University.

He worked at University College, London from 1960 to 1961 as an Honorary Research Associate, and at Northwestern University (USA) in 1961 as a research associate. He was a Visiting Professor of the University of Florence (Italy) in 1964, a Leverhulme Fellow at the University of Western Australia in 1972, and a Visiting Professor of the East China Normal University (China) in 1984.

He was a member of the Advisory Board of *Inorganica Chimica Acta* from 1967 until 1985, a member of the Editorial Board of *Coordination Chemistry Reviews* from 1982 to 1991, and Associate Editor of *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* from 1967 up to the present.

His spectroscopic studies on coordination compounds, especially on dichroism of the crystalline state, contributed much to the development of ligand field theory. He synthesized a great number of new metal complexes using Schiff base ligands to reveal interesting structural aspects in coordination chemistry of various transition metals. He is the author of some 200 research publications in inorganic chemistry.

S.K. Dr. Yamada, tell us why you chose the chemistry course at Osaka University.

I didn't think thoroughly about it. I had only a very vague idea about my academic speciality on going to university. In any event, I had been firmly determined to take a position in the university after graduation and continue fundamental scientific research as far as possible. In fact, a number of subjects in addition to chemistry attracted me on deciding the university course. One of the reasons why I finally decided to major in chemistry might be that in Osaka High School, which I was attending, there were excellent chemistry professors T. Tsumaki and M. Takebayashi. Indeed, numerous graduates from our High School, including a later

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Nobel prize laureate, Prof. K. Fukui, majored in chemistry at universities. As I learned later, Prof. Tsumaki had studied with Prof. P. Pfeiffer in Germany and discovered the oxygen-carrying property of [Co(salen)] in the crystalline state.

S.K. I think it was a very difficult period when you graduated from the university. How were you getting along in those days?

I graduated from the Faculty of Science of Osaka University with a B.Sc. in 1944 in the middle of the Second World War. During the war, the Japanese Government set up new "special graduate scholarships", which included exemption from military service, in addition to fairly generous financial support. Upon graduation, I was appointed a "special graduate student" and could continue my study at Osaka University under the direction of Prof. Ryutaro Tsuchida. The situation of the war, however, was getting more and more unfavourable to Japan and late in 1944, when the war was drawing to an end, the Tsuchida Laboratory had to be evacuated from Osaka to a small village at the foot of the northern Japan Alps, the very high mountainous area in the middle of the Japanese mainland. Young staff and several senior students, such as Kazuo Nakamoto and Akitsugu Nakahara, lived there together and spent every day reading and discussing research papers and monographs on coordination chemistry. The village people were very kind and warm to us, and the countryside in Toyama was beautiful with the Japan Alps in the background. It was not until the following summer, after the war was ended, that we returned to a normal research life in Osaka.

Professor Tsuchida was a man of a straight character. He was not only bright and intelligent but also sharp and creative, and used to stress to us the importance of originality in scientific work and also the spirit of pioneering research. If my memory serves me right, the Japanese students' primary objective at that time was to catch up with the West. It was then customary for the members of the Tsuchida laboratory to have lunch together in the professor's office, enjoying animated and frank conversation. I was often impressed, sometimes amazed, by his extraordinary and inimitable arguments, which were certainly unique and frequently even sounded extreme.

S.K. Tell us how you started your research at Osaka University?

As I mentioned earlier, I entered upon a chemical career in 1944 under the direction of Prof. Tsuchida who had published the results of his work on the "spectrochemical series" and also on the "coordination valence theory", which was the same as the VSEPR theory in principle but preceded it by several years. Then he had been carrying out vigorous studies mainly on electronic absorption spectra of transition metal complexes. In 1938, he and his co-worker, Dr. Masahisa Kobayashi, succeeded in constructing a novel apparatus for the measurement of crystal spectra, which consisted of a microscope and a spectrograph. This method enabled determination of electronic spectra and dichroism with a single microcrystal.

The research theme Prof. Tsuchida gave me was crystal spectra of coordination compounds with application to coordination chemistry. It was fortunate for me that I began my career with this theme, because there were very few chemists in the world who were able to produce crystal spectra of coordination compounds.

In those days, however, our laboratory, like other Japanese universities, was not well equipped and research funds were not at all sufficient. Moreover, scientific techniques, as well as theoretical aspects, were not sufficiently developed. For instance, the measurements of electronic spectra and dichroism had also to be carried out by the photographic method using a spectrograph, and consequently were much more troublesome and painstaking than they are now.

S.K. On what compounds did you run the studies with "crystal spectra of coordination compounds"?

I started the research with transition metal complexes having D_{4h} symmetry, such as *trans*-$[CoX_2(en)_2]^+$, $[PtX_4]^{2-}$ and so on, which were expected, judging from the symmetry of the complexes, to exhibit a distinct dichroism. Indeed, characteristic dichroism patterns were observed. It pleased me very much to find that some of them were reproduced later in some authoritative publications, such as *Gmelins Handbuch* and so on. As I remember rightly, it was about that time that I entered into correspondence with Dr. F. Basolo at the outset about absorption spectra of cobalt(III) and other transition metal complexes. He was so kind as to send me a small amount of his platinum complex. When I had a chance to meet him again later at a symposium, I mentioned it to him and thanked him, but he didn't remember it very clearly.

S.K. Then, you proceeded to compounds with metal–metal interactions.

Yes, in the next place, we turned to various coordination compounds with unusual colours, in which I had been taking a deep interest. For example, Magnus's green salt, $[Pt(NH_3)_4]$ $[PtCl_4]$, is coloured green in the crystalline state, whereas $[Pt(NH_3)_4]^{2+}$ and $[PtCl_4]^{2-}$ in aqueous solution are colourless and red, respectively. We determined the dichroism of Magnus's green salt by the microscopic method using a tiny crystal. A remarkable difference in the spectrum was observed between the *c*-axis (needle axis) direction and the direction perpendicular to it, leading us to propose a direct interaction between platinum(II) ions in arrays forming a one-dimensional chain structure $\cdots M^{2+} \cdots M^{2+} \cdots M^{2+} \cdots$ (type I). Studies were also extended to analogous related complexes, such as $Ni(Hdmg)_2$, $Pt(Hdmg)_2$, various copper(II) carboxylates, and so on (Hdmg denotes a dimethylglyoximate monoanion), and the possible existence of the metal-to-metal interaction was discussed.

S.K. You studied several complexes other than those you have mentioned. Which ones would you like to especially remark upon?

Metal complexes of another group in which I was very much interested were unusually deeply coloured compounds containing apparently tervalent platinum or palladium. For example, Wolffram's red salt, $PtCl_3(EtNH_2)_4 \cdot 2H_2O$, is coloured red as a solid and yellow in aqueous solution. We succeeded in determining the dichroism of this salt and of analogous compounds. Their dichroism patterns were more or less similar to each other. They exhibited strong broad absorption bands in the crystal needle axis direction, whereas no absorption was observed with light polarized in the direction perpendicular to the needle axis. We proposed a sort of interaction through halide ion between M^{2+} and M^{2+} ions forming the infinite chain structure, $\cdots M^{2+} \cdots X{-}M^{4+}{-}X \cdots M^{2+} \cdots$ (type II).

Among other compounds that had strongly attracted me were copper-coloured oxalato- and cyano-platinum complexes reported many years ago by Alfred Werner. The colour of their needle-like crystals was enchanting indeed with a bright lustre like metallic copper. The dichroism of the complexes we studied appeared to be closely similar to that of Wolffram's red salt and analogous compounds, leading us to assume an interaction along the chain structure of type II for the copper-coloured complexes. This assumption, however, turned out to be incorrect, as K. Krogmann disclosed much later. Using X-ray structure analysis, he showed that the complexes consisted of one-dimensional metal ion chains of type I, the platinum ions being equivalent and in a non-integral oxidation state.

S.K. In the late 1950s, you set up synthetic studies on complexes with Schiff base ligands. Perhaps you could tell us something about how you got started in the field.

While carrying out the research based on dichroism measurements, I eagerly read various research papers, including rather classical ones by past scholars, particularly A. Werner and his contemporaries, and was gradually attracted by synthetic research, in addition to the stereochemistry of metal complexes. As I told you, I had also marvelled at the strange property of [Co(salen)], which was reported to absorb and release a dioxygen molecule reversibly in the crystalline state. What kind of chemical bond is responsible for the combination of [Co(salen)] with O_2? What is the exact oxidation state of the cobalt oxygen adduct? And so on. With these problems in mind, I decided to take up Schiff bases obtained from salicylaldehyde derivatives and amines and to examine what structures and what properties occur in their metal complexes as we vary the metal ions on the one hand and the Schiff base ligand on the other. Late in the 1950s, together with graduate students, H. Nishikawa and S. Komorita (née Miki), I initiated such studies on metal complexes with Schiff bases and acid imides. There had not been many systematic studies reported on these complexes when we started the research. Moreover, the level of coordination chemistry in those days, both theoretical and experimental, was far lower than at the present day. We deliberately carried out the investigation with various metallic elements, including 4f elements. In the studies, emphasis was placed upon those complexes that involve uncommon structures, uncommon oxidation states, uncommon coordination numbers and uncommon properties, such as colour, magnetism and so on. Some of the main results were presented much later as a Section Lecture at the 13th ICCC in Zakopane, Poland, in 1970.

S.K. *You went to London to work with Professor Nyholm at the beginning of 1960s?*

Yes, it was 1960. I was very fortunate to have an opportunity to spend 18 months in Professor Sir Ronald Nyholm's laboratory at University College London. At University College, the research was very advanced in various areas of chemistry including coordination chemistry, and the chemistry department exhibited a lively and spirited atmosphere, which attracted many chemists from abroad to visit. Professor Nyholm was a man of very charming character with an outstanding genius in chemistry and always attracted people by his lucid and cogent discussion and animated conversation with wit and humour. During my stay there, I succeeded in synthesizing *cis*-$[CoX_2(diarsine)_2]X$ ($X = Cl$ and Br), which had been widely believed to be non-existent, only the trans isomer being in existence. Many things I observed and experienced there were fresh and exciting to me. Above all, my daily personal contact with Professor Nyholm and his splendid co-workers, including Drs. Tom Dunn, Jack Lewis, Brian Figgis, Barry Lever, Martin Tobe and others, was very important and precious for me. The scientific and cultural experience I was able to have during my stay in London was of inestimable value throughout the whole of my later life.

In 1961, after my stay in London, I took part in the 6th ICCC in Detroit. This was the first ICCC that I had attended and it gave me a good chance to meet many representative coordination chemists of the world, in addition to attending scientific sessions. Among others, I became acquainted with Professor Stanley Kirschner, later Permanent Secretary of the ICCC. Ever since, I have appreciated being on good terms with him and other distinguished chemists.

S.K. *When I visited Professor Sacconi in Florence in 1977, he told me "Yamada is one of my best friends". Would you tell us the story about Professor Sacconi?*

Just after the 8th ICCC in Vienna in 1964, I spent a few months in his laboratory in Florence, where energetic studies on Schiff base metal complexes were going on. I wanted to observe and learn how the active Sacconi group was pushing ahead. In his group there were a number of brilliant co-workers, such as Professors P. Paoletti, P. Orioli, M. Ciampolini, L. Sabatini, M. Di Vaira and others. Certainly we had plenty of time to discuss the current problems in the chemistry of Schiff base metal complexes, for example the five-coordinate cobalt(II) complexes of Schiff bases, which we had obtained in Japan. The five-coordination in cobalt(II) complexes was not so common as it is at present. Professor Sacconi and the members of his laboratory were very kind and accepted me warmly. He often took me to various institutes and plants he visited formally or informally. At half past ten every morning, we went out together to have a cup of espresso and on the way he used to teach me how to speak Italian. This gave me a good chance to learn how an Italian professor was doing things in research. I also often had lunch with Ivano Bertini and his beautiful fiancée (now Professor and Mrs. Bertini), who were also my good teachers of the Italian language. At the end of my stay in Florence, I managed to speak some Italian in daily life. Anyhow I got very fond of Florence, Italy and Italian people, so much so that every time I attended international meetings in Europe afterwards I tried to visit Florence again in order to meet Italian friends and learn about the progress in coordination chemistry there.

S.K. As you had a special interest in [Co(salen)], tell us just briefly about your studies on salen complexes. Among the complexes you synthesized, you must have some that you wish especially to remark upon.

In connection with the intrinsic oxidation state of cobalt in the dioxygen adduct of [Co(salen)], we prepared definitely tervalent cobalt complexes of the type $[CoX_2(salen)]Y$ and the corresponding chromium(III) complexes. Some of the other noteworthy salen complexes we prepared were $[Ce(salen)_2]$ and $pipH[Ln(salen)_2]$, and $[MoO_2(salen)]$ and related molybdenum(VI) complexes (pipH = the piperidinium cation, Ln = the lanthanoid ion). The mononuclear eight-coordinate structure of the lanthanoid(III) complexes was confirmed by X-ray. It is interesting that quadridentate salen in $[MoO_2(salen)]$ is forced to be distorted considerably from planar configuration, since the MoO_2^{2+} tends to be bent with an O–M–O angle of about 90°.

S.K. You also studied extensively complexes with bulky bidentate Schiff bases. In those studies you have shown various stereoisomers for the four-coordinated nickel(II) and copper(II) complexes.

We have made strenuous and deliberate efforts to examine the steric effect of the ligands bearing a bulky substituent on the structure of metal complexes. Let me mention interesting examples. The normal structure for $Ni(X\text{–}sal\text{–}R)_2$ and $Cu(X\text{–}sal\text{–}R)_2$ is square-planar or nearly planar (X–sal–R is a bidentate substituted salcylaldimine). With R = isopropyl (i-Pr) or cyclohexyl (Ch), however, the steric constraint becomes so marked as to make the structure of the metal complex distorted from normal. We finally succeeded in isolating a number of planar and pseudo-tetrahedral isomeric pairs of $Ni(X\text{–}sal\text{–}R)_2$, and also examined interconversion between the two different configurations, (R = i-Pr; X = 3-NO_3, 3-CH_3O, 5,6-benzo, 3,5-Br_2 and R = Ch; X = 5-Cl, 5-Br, 3-NO_2, 3-CH_3O, and so on). Before our work was published, it had been widely believed that only one isomeric form, either planar or pseudo-tetrahedral, could be isolated as crystals for these complexes, depending upon the nature of R and X.

In the case of copper(II) complexes, we also isolated various stereoisomers having configurations with different degrees of distortion, in addition to the planar and binuclear ones. They seem to exist in equilibrium in solution.

S.K. Looking back on your academic life, would you give us some comments?

First of all, I wish to note that I had many excellent co-workers and graduate students, including Dr. Wan Songping from China, who were involved in the studies mentioned above. I'd like to give them specific credit, but this, to be complete, would be too long. In the following only some of them are cited, to whom I am very grateful: Drs. H. Nishikawa, S. Komorita, K. Yamanouchi, Y. Kuge, A. Tekeuchi, and H. Kuma (in chronological order).

Turning to the past years, I think I was fortunate in various aspects. It is a great pleasure to me that I was able to work in the exciting and interesting period called the renaissance of coordination chemistry, when coordination chemistry was making rapid and remarkable progress, although I certainly wish I could have contributed much more in my capacity. Japanese coordination chemistry has also made great strides since I started my career nearly 50 years ago. In fact, Japanese coordination chemists have increased in number enormously, publishing now many more papers in various journals than in former days. The current state of Japanese coordination chemistry, however, is not fully satisfactory, and it is generally agreed, by many researchers in this field, that extensive reformation and improvement are desirable not only in the field of coordination chemistry but also in the whole area of chemistry. An excellent critical survey about the state of chemistry as a whole in Japan was published recently by K. Nakanishi (Chem. Eng. News., Dec. 2 (1991) 30). As discussed therein, "Japan is in the midst of planning or implementing drastic changes in its antiquated educational and research work". Optimistically speaking, things will go forward better in the long run if proper action is taken to improve the present state in an extensive and drastic manner. Various complicated and difficult factors, however, are involved in the matter, and I am afraid that it will take a very long time for noticeable changes to be realized.