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Interview of Professor Gallais for the special edition of Coordination Chemistry Reviews Inorganic Chemistry in France

Pierre Braunstein: Prof. Gallais, this year you celebrated your 90th birthday. This is indeed an excellent occasion to share with us some of your recollections, particularly because your memory remains remarkably sharp. Shall we start our discussion with the family environment of your childhood and your precocious attraction to the sciences, and to chemistry in particular?

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Fernand Gallais: As the son of parents of modest standing, I grew up in an environment where education was a religion. My father held unlimited respect for those people who were actors in the fields of science. We must remember that science and technology had an important impact on the public because of their considerable role during the First World War. Submarines, explosives, military gas, the development of the automobile and the railroad, the progress of medicine,... all this contributed to arousing the public's curiosity in science. My education was directed towards the sciences, although I also studied Latin and Greek, for which I held a passionate interest. At the Lycée Henri IV in Paris, the attitude of the teachers and their love for the profession impressed me. They never dressed in an everyday style nor as tourists, but rather would wear a black jacket with striped trousers, wing-collared shirt and tie–almost formal evening dress–which inspired respect and encouraged the sharing of their love for the subjects they taught. I was very glad to have had a scholarship because at that time they were few, and the qualifying exam was very severe. My studies led to the Baccalauréat degree in “Elementary Mathematics”, as well as in “Philosophy”, which I received in the same graduating class.

The choice of a scientific career was strengthened by my good results at school and by my strong personal taste for chemistry experimentation. Even at my parents' house, I was sometimes responsible for the appearance of bromine fumes or the tossing of calcium phosphide into puddles on the balcony–a stupefied sight for my mother and my aunt as they watched flames emerging from the water ! Also, a distant relative, who had studied as a pharmacist, took me to visit the various departments of the hospital where he was an intern. All these factors influenced my decision to study pharmacy, taking into account the scientific and, above all, chemical aspects that seemed to me important for this profession, as well as the possibility to pursue an independent career.

P.B.: You seem to clearly feel a vocation for science and, in particular, for chemistry. How did your later studies and the beginning of your professional career develop ?

F.G.: In fact, I wanted to be active in science and thought it necessary, at a time long before the birth of the Centre National de la Recherche Scientifique and when the doors of Higher Education were just begining to open (there were only 6 chemistry professors at the Sorbonne and about 15 universities in France), to secure a diploma that would allow me to pursue a career less uncertain than those in teaching and research. I chose to become a pharmacist because much of this activity is devoted to chemistry. But the moment it was possible, I went to the Sorbonne in order to learn more about the discipline that I was already truly fond of. It was there that I was captivated and influenced by several professors, but above all, by two of them, Georges Urbain and Paul Pascal. The impact of Professor Urbain's teaching was of great importance. I can still see him with his magnificent head of grey hair and his artistic allure ... He was a leader in his field in France. His book “Introduction to the Chemistry of Complexes”, published in 1913, had a very strong influence on me, as did his lectures. At that time, there was no talk of “coordination chemistry”. In addition, we never really wondered about the basic nature of the chemical bond nor about the profound meaning of the lines we drew as bonds in the molecular formulae of organic and inorganic molecules; this lack of understanding unquestionably motivated my later research. During the 1930's, the teaching of physical chemistry was dominated by thermodynamics and that of chemistry by organic chemistry. It must be said that the influence of the Nobel-Prize winners Grignard and Sabatier was of course considerable, but additionally, eminent scientists such as Curie, Langevin and Perrin, who had very strong ties, exerted a most significant influence on the actors of science and opened entirely new horizons. I would like to recall in passing an anecdote that demonstrates to what extent French chemistry had become stiff and indifferent to the theoretical progress that had been realized since 1900 elsewhere. While I was a student at the Faculty of Pharmacy in 1928-29, I took a course in General Chemistry, given by an expert in the subject area who was at the same time a professor at the "Ecole Polytechnique". This was Mr. Charpy, who had published an excellent treatise on inorganic chemistry with his colleague Mr. Gautier and who, in formal attire, provided a full semester of education that would have been imaginable at the beginning of this century. But he left out entirely the revolution that had taken place since, to the point of dedicating only two weeks to discuss in fine detail what he called "the atomic theory" !

After obtaining my degree in physical sciences in 1934, I defended a doctoral thesis in pharmacy in 1935 and received my "Doctorat d'Etat" in physical sciences in 1938. As the years went by, I was increasingly convinced to pursue an academic career and the hope to try to model myself after the professors at the Sorbonne. After 5 years as an intern in pharmacy, I was appointed head of laboratory at the Faculty of Medicine in Paris, a function that I exercised for 7 years. The time I spent at the Faculty of Pharmacy and in hospitals allowed me to become close to several great chemists, in particular Professor Paul Lebeau as well as my friend Professor M.M. Janot. I also remember vividly and with admiration the great medical doctors with whom I worked during these years. They were all remarkable: Drs. Achard, Labbe, and Harvier–but it was certainly Dr. Achard who impressed me the most. As he approached his 75th birthday he still demonstrated a lively intelligence that made him a clinical doctor difficult to equal. Quite rapidly, I found the means to carry out my work. In the laboratory that Professor Achard entrusted to my responsibility, as in those of Professor Goris and at the pharmacy of the Cochin Hospital in Paris, my taste for research strengthened and developed freely. This long, daily contact with clinical medicine facilitated the future task of working in the CNRS directorship, where I was responsible in particular for medical research for eight and a half years.

P.B. How did these first years of research go ?

F.G.: During this period, I carried out some limited work in analytical and biological chemistry, as well as my first research in inorganic chemistry and in physical chemistry. Being, in the beginning, rather isolated, I was profoundly influenced by the education I received at the Sorbonne and by the personalities of those who offered it, as I mentioned already. Professor Georges Urbain provided the inspiration for my thesis topic, which I selected myself, and he passed on to me his taste for inorganic chemistry. Thus, it is hardly suprising that, in 1932, as soon as I obtained some results on mercury complexes I wanted to present these to Prof. Urbain, whose lectures and writings had raised my enthusiasm for the work of Alfred Werner. The open and kind attitude and the encouragement he showed to me on this occasion were to prove decisive for me, and I consider it an honor to have been one of his last disciples. The orientation of my research towards the problems of structure in inorganic chemistry led me to benefit from the kind advice of Professor Aimé Cotton, and of Professor Paul Pascal, whose support afterwards proved to be so valuable.

I had in fact studied the magnetic properties of mercury complexes and determined that those derived from mercuric iodide were radically diamagnetic, whereas Paul Pascal, a few years earlier while he was in Lille, had obtained the opposite result. Professor Urbain encouraged me to talk to him about this, so I went to see him just before defending my thesis. Strongly impressed by his personality, I was greatly relieved when, following our discussion, Prof. Pascal told me that I was certainly right. I began to develop stronger relations with him, and this is the reason he agreed to write, much later, the preface of my book entitled “Theoretical and Experimental Inorganic Chemistry”.

My more intimate contact with physics derives from the fact that I rapidly needed to carry out measurements on magnetic rotation; thus, I developed friendly ties with Professor R. Lucas at the School of Physics and Industrial Chemistry, who offered me his inexhaustible support. And finally, physics allowed me to get to know the large electromagnet laboratory of the Academy of Sciences in Bellevue, as well as its Director, Professor Gaston Dupouy, in order to carry out measurements on magnetic susceptibility.

In June, 1940, I was demobilized and sent to Toulouse, returning to Paris in November as Head of laboratory at the Cochin Hospital (Faculty of Medicine) and as a member of the Faculty of Pharmacy. I remained there until the autumn of 1942, when I was named “maître de conférences” (i.e. lecturer)at the Faculty of Sciences in Toulouse. Professor Gaston Dupouy who held there the chair of Henri Bouasse had told me that this position was available. I had no hesitation to join him and to leave my position at the Faculty of Pharmacy in Paris because I knew that, with him, I would find all the moral and material support I would need, and which he did in fact lavish upon me.

P.B.: So, at this point in time you arrive in Toulouse. How did your work and various other activities progress?

F.G: For ten years I lived in a small requisitioned house with my family, after which I bought some land and had the house built that I still live in. From a professional perspective, I found myself in a very small faculty, with a council of 15 members, over which an exceptional sense of solidarity and friendship reigned, particularly compared to what one sees today. As for the students attending the courses, this was quite a pleasant situation because they were reasonable in number and very happy to have a class which covered material that had not been taught since the death of Paul Sabatier two years before. It was in fact Paul Sabatier who, in his retirement, had continued to teach inorganic chemistry. Otherwise, I found an office and a small laboratory for my personal use, both completely empty. I was able to establish good relations with most of my colleagues and, in particular, with a professor of mechanics, Mr. Roy, who came from the old school and with whom I had a very pleasant relationship. This friendship opened the horizons to a life that could be described as that of a provincial professor before the war. Receptions were held regularly in our homes for the colleagues and their families. These were naturally very convivial but also instructive; this was how I met and developed friendships with people such as the Rector Deltheil–another example would be the director of the Observatory Mr. Paloque–and also how my family developed its relationship with the family of Mr. Dupouy.

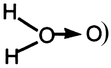
When Professor Georges Mignonac gave me the responsibility, in 1943, to teach Inorganic and General Chemistry, I was required to build a research unit under unfavorable circumstances. After being named Professor (without a Chair) in 1947, I became full Professor in 1951. After the war, I remember two very important CNRS colloquia organised by Bauer and Pascal, at which eminent scholars such as Mulliken and Pauling presented their work. These contacts and meetings were of utmost importance during a period when international exposure was not yet in France what it would become. In 1950, I took over the direction of the Institute of Chemistry in Toulouse, which had been created by Paul Sabatier, and had the satisfaction of seeing it transformed, in 1953, into an “Ecole Nationale Supérieure d’Ingénieurs”. On the other hand, it took many years to build my research unit into the group that exists today and which, in addition to forming a complete department from 1965 -1970 has given rise to two associated research units within the CNRS.

The more important of these laboratories in size is the Laboratory of Coordination Chemistry, which I founded and directed as of the first of January 1974, and which became a full CNRS laboratory. R. Wolf, M. Durand, and G. Jugie were among its researchers, and the research groups included those of J.P. Laurent, J.F. Labarre, Ph. De Loth, D. Voigt, P. Cassoux, Y. Jeannin, R. Poilblanc, J. Galy and D. Gervais. A large quantity of equipment, accorded through successive national research plans, was put at our disposition, which meant that we had access to essential installations for the physical aspects of our studies (Faraday effect, diamagnetism, nuclear magnetic resonance, etc.). But the implementation of new techniques became rapidly necessary (electronic spectroscopy, quadrupole nuclear resonance, microwave spectroscopy, theoretical chemistry, etc.). Thus, the technical staff had to be increased so that the various research groups could take full advantage of this situation.

The second research unit that emerged from the Department of Physical and Inorganic Chemisry was the team run by Mr. Montel, the Laboratory for Solid-State and High-Temperature Chemistry. This unit was closely related to the special Metallurgical Service created at the National School of Chemistry, which became part of the National Polytechnic Institute of Toulouse. This team’s activity, and the research of the groups of Poilblanc, Jeannin and Galy, nicely complemented locally the work that I had personally instigated. I maintained my initial orientation towards structural problems in inorganic chemistry, but most often this led me to study structures containing a small number of atoms (dissolved complex ions or discrete molecules in the liquid state) rather than the larger aggregates which form crystalline networks. In order to solve these types of problems, I had to introduce various physical methods, whereas the interpretation of these results led me gradually to the study of the nature of the chemical bond, that is, towards certain aspects of theoretical chemistry.

Among the physical methods used, the measurement of the magnetic rotation appeared as primarily important. The Faraday effect, well studied in France by Professor R. de Mallemann, was mostly of interest to physicists, and despite the promising results obtained a half century earlier by Perkin, chemists were not interested in this effect, perhaps because of the complicated experimental set-up required. I made efforts to explore the application of the Faraday effect to chemistry, and I was happy to show, with my co-workers, that this field was rich with a variety of possibilities.

After applying this technique, by the method of continuous variations, to the study of the formation of many Werner complexes, particularly those proceeding from mercury (II) iodide and thiocyanate; bismuth (III) iodide, thiosulfate and thiocyanate; copper (II) nitrate and thiocyanate, I showed that it is possible to use it to study the progress of reactions in solution. We then determined that the Faraday effect of an atomic structure is very much influenced by the set of coordinating and multiple bonds that it contains.

One interesting illustration of this phenomenon was the demonstration in the laboratory that certain inorganic acids do not exist in the state that one would suppose based on the name they are referred to. This is particularly true for thiocyanic acid, which is in reality the first term in the senevol series, and for phosphorous acid, indeed the first term in the series of phosphonates. Another important result was to establish that in hydrogen peroxide and in other peroxy acids, the additional oxygen atom that brings about the peroxy character is not coordinated, and that it simply inserts itself into the X-O-H chain in question (e.g., H-O-O-H for hydrogen peroxide rather than ). It also became evident from these studies that within the molecules of strong oxyacids, there is always at least one oxygen atom bound to the central atom by a dative bond, thus increasing its electronegativity and providing an explanation for the strength of these acids.

In fact, magnetic rotation turns out to be a quantity that is very sensitive to the state of the chemical bond and can be determined with great precision. This opens two pathways for its use, the first of a practical nature which consists of establishing a systematic set of measurements related to bonds that would be useful for the study of molecular structures (like the systematic classifications used in refraction and magnetism); and the second of a theoretical nature which consists of studying how the contribution to the magnetic rotation of a bond is related to its particular state, with the goal of turning this technique into a general method for the study of the chemical bond.

In both cases, we were able to make good progress. At first, we were able to show that the measurements based on bond type are, apparently, constant enough in organic chemistry to permit systematic classification, and we gave values for the bonds that are commonly found in the aliphatic series. Once this was done, we returned to inorganic chemistry and undertook the systematic study of the σ bonds found in the compounds of boron, nitrogen, sulfur and phosphorus. For each of these series we succeeded in providing lists of bond rotations from which molecular rotations can be calculated, a priori, in a satisfactory way. The existence of this systematic classification scheme was later justified theoretically in the framework of Dandel's "Loge theory". This classification should be considered, however, as a first approximation. This is because we have shown that the rotation of a bond, far from being a true constant, is a function of the partial ionic character of the bonds. Thus, the possibility of applying this systematic classification depends on the mechanisms of intramolecular compensation, whose nature we defined, thereby allowing us to specify the limits of applicability.

I would nonetheless mention that this led us to propose a method of "rolling iterations", applied first to one center and then to several. Beginning with the electronegativity of isolated atoms, one can evaluate the electronegativity of groups and describe the real state of all the bonds in a covalent molecule, as well as the formal charge distribution within that molecule.

In addition, we established that the formation of a donor-acceptor bond is most often accompanied by a large, negative increment in the rotation (to which there is no corresponding paramagnetism) whereas the Π-electrons of multiple bonds turned out to be excessively active. These properties led us to develop a new technique:

(a) For the study of multiple bonds and of conjugated systems. We find in organic chemistry that the $C=C$ double bond has a very constant increment of 136μm, with a Π-bond contribution of 117μm, and that the acetylenic $C+C$ bond has an increment of 174μm with a Π-bond contribution of 155μm. We should add that for compounds composed of multiple conjugated bonds, with delocalisation of the Π-electrons, the magnetic rotation turns out to be further enhanced (110r for a diene and 77μm for a diyne).

In this respect, there is particular interest associated with the arenes. In this case the laboratory results obtained led to the proposition of an original definition of the concept of "aromaticity", by indicating the conditions under which the ring current, responsible for the aromatic properties, can form. The general character of this definition allowed us to tackle the problem of aromaticity in inorganic ring systems (borazines, boroxines, etc...) and to determine in each series a scale of aromaticity.

(b) Towards the detection and study of dative bonds whose importance is confirmed by a good fraction of modern chemistry. This point is essential in our opinion; it led us to propose a program of cooperative research devoted to the bonding in coordination compounds involving both s- and p- electrons (with Mrs. Josien, M. Bigorgne, Daudel, Paris, Souchay and Tirouflet). This program culminated in an international colloquium that took place in Paris in October 1969, in which a long series of results was presented on the nature and the properties of the donor-acceptor bond.

We were above all able to show, on this particular occasion, to what extent the relationship between the Faraday effect and coordination is important. Thus, for example, the oxides of tertiary amines R_3NO have a molecular magnetic rotation inferior to those of the parent amines; this difference is -40μm for the oxide of triethylamine in spite of the increase of molecular mass due to the additional oxygen atom. This is also the reason why the coordination of Lewis bases to boron trifluoride, BF_3, is associated with negative changes in the magnetic rotation that vary, for nitrogen-containing bases, from -506μm (base R_3N) to -33μm (base NH_3), and for oxygen-containing bases from -355μm (base R_2CO) to -320μm(base RCO_2H).

Afterwards, the semi-empirical "rolling-iteration" method allowed us to study the real state of a bond, i.e., its fraction of ionic character and, by consequence, the charge transfer that accompagnies its formation. It was found that this transfer is indeed much more important for a coordination bond than for the formation of a normal covalent bond, but that it is still far from reaching the situation implied by the classical formulas $D \rightarrow A$ or D^+A^-. The theoretical studies of Daudel, Veillard, and Aslangul have confirmed that the value of this transfer is on the order of 0.25e to 0.30e and that this transfer takes place from the entire donor group towards the acceptor group (and not only from atom D to atom A).

Finally, we must stress that, for all the above, the Faraday effect has been applied almost exclusively in the spectrally transparent region. This is no longer the case for certain developments that have taken place afterward, carried out on compounds that absorb ultraviolet, or even visible light and for which an abnormal, but well-determined dispersion plays a major role. The study of this dispersion must be a priority; new perspectives can be opened by relating this dispersion to that of circular dichroism. This is particularly the case for certain derivatives of transition elements; these have provided us with several substances that are characterized by apparently singular properties, to start with because they have the opposite sign of magnetic rotation with respect to water, even though they are strongly diamagnetic on the molecular scale. We have been able to add about 20 examples of this phenomenon to the list of the two or three that have been known for a century.

In any case, in the field of the applications of the Faraday effect to Chemistry, the Toulouse laboratory has played a pioneering role for quite some time. It is certainly for this reason that I have been frequently called upon to present the results that were obtained there (Paris, Bordeaux, Lille, Montpellier, Bonn, Liège, Oslo, Stockholm, Uppsala, Vienna,...)

In conclusion, I would like to stress that the fundamental theme of my research has always remained coordination chemistry, even if the Faraday effect has played an extremely important role. From the experimental determination of the formula of the mercuriiodides to the theoretical study of the nature of the $N \rightarrow B$ dative bond in aminoborane ammoniacate, the line of my research has been straighter than it might seem after the first glance.

Please allow me, in addition, to pay homage to the international organizations that have given me the opportunities to speak in front of and, above all, to learn from outstanding "areopagus". The IUPAC immediately comes to mind, whose conferences I attended from 1947 to 1970 and for whom I worked, alongside my dearly missed friend Professor J. Chatt, as co-secretary of the Nomenclature Committee of Inorganic Chemistry from 1959 to 1971. Then I think of the International Conferences on Coordination Chemistry, where again, I had the chance to build a friendship while working with Professor S. Kirschner, between 1965 (St. Moritz) and 1986 (Athens), via Toulouse in 1980.

P.B.: You were able to reconcile your activities in research, teaching and research administration at the highest levels during the eight and a half years that you were Adjunct Director for Natural Sciences and then Scientific Director of the CNRS. Could you tell us something about this period ?

F.G.: Since 1943, I have had to reserve a good part of my activities for teaching and administration. I was approached to publish a book in 1950 on "Theoretical and Experimental Inorganic Chemistry: Electronic Chemistry", which at that time seemed to answer a real need. This book was essentially an essay on inorganic chemistry, presented in a rational and systematic manner, with the aim of rousing students' interest for a discipline that was too often represented as being in its final, stable phase. The first volume of the second edition appeared in 1963.

I also published, in collaboration with G. Rumeau in 1958, "General Chemistry", written for candidates aspiring to obtain an entrance to one of the French "Grandes Ecoles". This book conformed with the modern program outlined by the Chatelet Commission and was the beginning of a collection of books on the subject of Chemistry.

Finally, in January 1965, I was called to the Direction of the Centre National de la Recherche Scientifique, first as Adjunct Director for Natural Sciences (with Mr. Jacquinot), and then as Scientific Director. In the latter role, I specifically followed the research that was carried out in the areas of chemistry and bio-medicine. The initial scientific scope was vast and exciting, stretching from mineralogy to medicine. I was able to keep frequent company with J. Monod and A. Lwoff, future Nobel-prize winners in Medicine, and to propose to the latter that he assume the direction of the CNRS cancer laboratories in Villejuif, where more that 400 people worked.

It was at the end of this mission that the CNRS entrusted with me the task of creating, in January 1974, and directing until my retirement, in October 1978, the very same laboratory in Toulouse dedicated to Coordination Chemistry that we have already discussed.

P.B.: After having been elected Corresponding Member of the Academy of Sciences of Paris, in 1966, and then Member of that Academy in 1973, you were President of the French Society of Chemistry from 1978–1980, not to mention your role in several other eminent functions. Would you like to say something about this ?

F.G.: It is true that I heartily defended the cause of Chemistry whenever the opportunity presented itself, at the Academy or elsewhere. Concerning the Chemical Society in particular, I had to struggle with its Journal–and by the same token with many society members–against the handicap created by the exclusive use of the French language !

It is very comforting, on the other hand, to see the position that the French Inorganic Chemistry now occupies and its audience on the international scene. This special edition of Coordination Chemistry Reviews, dedicated to this community, is after all a beautiful illustration of this achievement.

P.B.: Prof. Gallais, I thank you very much for having shared your memories with us, even though the lack of space has forced us to leave aside many questions.