

RETROSPECT AND PROSPECT: 25 YEARS OF THE I.C.C.C.

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Abstract - Events leading to the establishment of the International Conferences on Coordination Chemistry and early parallel development of complex chemistry in the author's laboratory are reviewed with some reminiscences of the earliest conferences. This is followed by consideration of a few recent developments and a projection into the future.

The 25th Anniversary of the first International Conference on Coordination Chemistry (I.C.C.C.) occurred last year, but since there was no conference then we are celebrating it at this meeting. I have been asked to say something about the beginnings of the I.C.C.C., and the development of complex chemistry over the last quarter century and into the next. Developments over the whole area of complex chemistry have been too vast for an adequate summary to be made in a one-hour lecture. It would sound too much like a reading of 'Chemical Abstracts'. I think therefore that I can best comply with the request with which you have honoured me by saying something about the early conferences and about the developments in my own area of complex chemistry.

RETROSPECT

In the 1950's and 1960's there was an explosion of interest in complex chemistry which Professor Nyholm has called "the renaissance of inorganic chemistry". But the seed had been sown for this rebirth during the 1930's. Werner's ideas on the structures and stereochemistry of complex compounds were well established but imperfectly known to the vast majority of chemists. The apparent constancy of the coordination number at either four or six and very rarely anything else, the lone pair theory of coordination which had developed from G.N. Lewis's electron pair bonds, N.V. Sidgwick's propagation of that theory and his effective atomic number (E.A.N.) rule had brought unifying principles to coordination chemistry and, by applying those principles, the experimenter was often able to fit a structure to his compounds. His only firm information concerning this structure was provided by the method of preparation, the elemental analysis of the compound, and often its property as an electrolyte. Sometimes the classical methods of organic structure determination, that is the replacement of one group by another to give compounds of known configuration, was used to determine configuration. Such methods could only be firmly applied to the most robust of complexes. Thus although the bridging of metal atoms by halogen atoms had been postulated and structures set out with such bridges, their lability was such that their existence was still a matter of conjecture. Many chemists could not be persuaded that a monovalent atom like chlorine could possibly form two bonds linking together two metal atoms. Others were just as convinced that it could.

The way was paved for the rapid advance in inorganic chemistry by the development of physical methods of structure determination, by the measurement of dipole moments and magnetic moments, and more than anything else by the development of structure determination by X-rays. It had just reached the stage at which it was possible to apply the method to crystals containing rather complex molecules, such as those of coordination compounds. The determination of a structure was long, and could take from one to three years. Nevertheless it allowed coordination chemists to check

some of the basic types of linkage, such as the halogen bridge. It also allowed for a few false starts, such as the demonstration that trimethylplatinum iodide had a tetrahedral configuration! Electron diffraction came to the aid of those who dealt with volatile compounds, such as tetracarbonylnickel which in my school book was given the structure in Fig. 1. The structure serves as an illustration of the confusion which

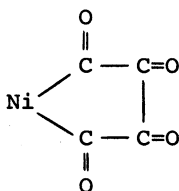


Fig. 1

existed in many chemists' minds between valency and oxidation state, and also of the scant regard most chemists had for coordinative saturation, for surely divalent nickel should have a coordination number of four or six, certainly not of two? By 1939, because of the groundwork done on X-ray crystallography, the determination of definitive structures of complex compounds was a subject ready to fly, but it was not until after the war that it could really take wing.

By the time it did take off, infrared spectroscopy was becoming the tool of the preparative organic chemist. Ligand field theory was leaving the realm of physics. The use of organic ligands to produce coordination compounds soluble in organic solvents had taken hold, and many of the methods of organic chemistry could now be applied to coordination chemistry. Nevertheless there were not many protagonists of coordination chemistry, and the few there were got little support from the vast number of chemists who regarded coordination compounds as of little interest or consequence.

There was one set of ligands which in no way appeared to fit the lone electron pair theory of coordination. These were olefins in complexes such as Zeise's salt, $K[PtCl_3(C_2H_4)]$. Their existence intrigued me and I set about finding how the olefin was attached to the metal because, although I believed in the general applicability of the lone pair theory, I also felt that the existence of olefin complexes meant that the theory was not complete. This was the first problem on which I worked when I was freed from war-time duties in 1946. How little it interested many other chemists is illustrated by the remark, around 1950, of a chemist (not inorganic) who has since become a Nobel Prize winner. He said "It's a nice little field you've carved out for yourself Chatt, but" and he indicated that he didn't think there was much to it. It was in this atmosphere of frustration that the first conference on coordination chemistry was conceived.

THE FIRST CONFERENCE

The first I.C.C.C. was held on 21st-22nd September 1950 at the laboratories of my employers, Imperial Chemical Industries Limited, who also financed the conference. It was attended by 32 delegates from outside the Company and the total attendance was not more than 40. The fifth I.C.C.C., in 1959, was the next one to be held in the U.K. So rapid had been the growth of interest in coordination chemistry that the 1959 conference had a total registration of about 750.

The conferences on coordination chemistry thus arose from my frustration as a young coordination chemist who found his subject ignored by all the national societies concerned with chemistry. Many chemists knew nothing and cared even less about it. It was difficult to find someone with whom one could discuss complex chemistry. It had never been popular in the English-speaking world and I may take the view of my schoolmaster, an excellent teacher, as typical. To him, coordination chemistry meant cobaltammines, those mysterious and useless substances whose structures had

been explained by a European chemist named Werner. The ideas which had earned Werner a Nobel Prize had not stirred the interest of any except a very small number of British chemists. I had the good fortune to work for my Ph.D. in Cambridge (1937-1940) under the guidance of one of them, Dr. F.G. Mann, who introduced me to the existence of ethylene complexes and gave me a very good grounding in complex chemistry, a grounding such as I could have received from few others.

As I have said, olefins differed from all other ligands in that they had no lone pair of electrons on any possible ligand atom. There were some rather fanciful formulae, such as that in Fig. 2, going around at the time. Olefins were not treated as normal ligands and I decided that these anomalous ligands, if their bonding to a metal could be understood, would point the way to some very interesting chemistry.

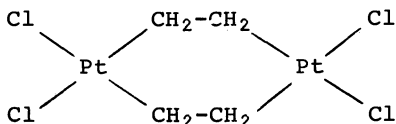


Fig. 2

My work on this topic really got underway when I joined the new laboratory established by Imperial Chemical Industries Limited at "The Frythe" near Welwyn Village in Hertfordshire. The company considered that the sort of chemistry I wished to do would be of interest to the petrochemical side of their activities. At that time most chemists did not even know that olefins had a coordination chemistry. My frustration in not finding other chemists with whom to discuss the subject led me to complain to the manager of the laboratories, Mr. M.T. Sampson, that there were never any meetings to discuss coordination chemistry. He replied "Why don't you organise a meeting yourself?" When I said that it would cost money he promised to finance it from the laboratory's budget. I discussed the idea with Dr. R.G. Wilkins, who had recently joined me as my first post-doctoral co-worker, and we decided to organise a symposium on coordination chemistry. We had no thoughts then of it growing into an international periodic occurrence.

So Wilkins and I went through the pages of the Journal of the Chemical Society and we picked out everyone in the U.K. who had done anything at all in the field of complex chemistry since about 1930. We invited those who had recently been most active in publication to present papers and we invited all others available to participate. Only two people attended from overseas - Professor K.A. Jensen, because we had long admired his work on platinum(II) complexes, and Professor G. Schwarzenbach, because he was publishing a great amount of work on stability constants and happened to be in England at that time. He was also very well known to Mr. Sampson. Dr. R.S. Nyholm and Professor A. Albert were in England; both had Australian connections and were invited. The symposium was a great success and its Proceedings were summarised in Nature. The detailed Proceedings appeared simply as a report of Imperial Chemical Industries Limited (Butterwick Research Laboratory, Report No. BRL/146) in May 1951 and a few copies have gone into national libraries. The conference lasted two days, there were no parallel sessions and nine papers were given.

The general introduction to the conference was given by Professor N.V. Sidgwick at one of his last public appearances. The summing up was by Dr. L.E. Sutton. The papers given were as follows and show the areas of interest to coordination chemists in the U.K. at that time.

General Introduction to Coordination Chemistry	Prof. N.V. Sidgwick
The Complex Derivatives of the Tertiary Phosphines and Arsines with Mercury and Cadmium	Dr. F.G. Mann
Stability Constants of Chelate Complexes	Prof. G. Schwarzenbach

The Stability of Coordination Compounds in Aqueous Solution and the Varying Strengths of Metal-Ligand Bonds	Dr. H. Irving
Complexes of Some Lighter Transition Elements with a Di(Tertiary Arsine)	Dr. R.S. Nyholm
The Coordination of Olefins to Platinous Salts	Dr. J. Chatt
Cis-Trans Equilibria in the Platinous Series of Compounds	Dr. R.G. Wilkins
Some Aspects of the Stereochemistry of the Coordination Number Five	Prof. K.A. Jensen
The Significance of d-Orbital Hybridisation in Coordination Compounds	Mr. L.E. Orgel
Coordination Groups of Atoms in Crystals	Dr. A.F. Wells
Summary	Dr. L.E. Sutton

I put forward the view, which I had expressed a few times before, that the phenomenon now known as back bonding was the essential feature of the binding of olefins to transition metal ions (Ref. 1), but I had difficulty deciding which orbital on the olefinic ligands received the d -electrons from the metal. Because platinum and palladium complexes produce acetaldehyde on reaction with water, I suggested that the complexes were in fact ethylidene complexes. These would now be named methylcarbene complexes, and the structure I suggested at the first I.C.C.C. is given in Fig. 3. Shortly after this, Dewar (2) suggested that the antibonding orbitals of the olefin were the recipients of the d -electrons in silver olefin complexes and eventually when our laboratory got its first infrared spectrometer Dr. L.A. Duncanson and I were able to show that the olefin in platinum(II) complexes did indeed remain essentially unchanged, and we put forward the well-known structure shown in Fig. 4 (Ref. 3).

In my preface to the report on the meeting I started by pointing out that the conference was a unique occasion and finished by saying that I hoped it would be the forerunner of others. I had no thought that it might be running 25 years later, and still running very strongly. Professor K.A. Jensen obviously enjoyed the meeting because he said that it was a small, very pleasant meeting of the kind which the rather small Danish Chemical Society could very well organise. He proposed that the next meeting should be held in Copenhagen, and we owe the propagation of the conferences to him. It took 3 years to obtain finance and organise that second conference, which was held in Copenhagen on August 9th-13th 1953. The Proceedings were published by the Danish Chemical Society in 1954, and the organising committee was R.W. Asmussen, Jannik Bjerrum, and K.A. Jensen.

THE SECOND CONFERENCE

The second conference was much more international in flavour. In addition to the Danes, there were 59 foreign participants, mainly Swedish, British, German, American, Dutch and Italian. Its European character was so marked that the President, Professor Asmussen, referred to it in his opening remarks as the "second European symposium devoted entirely to coordination chemistry". Thirty-two papers were given at that conference. There were no parallel sessions and no plenary lectures except that Professor Niels Bjerrum gave a very interesting introductory lecture. It was interesting to me because Niels Bjerrum had worked with Werner in Zurich and was able to say something about the way in which Werner worked. This was also my first conference abroad in a non-English speaking country and I never ceased to be amazed at the number of languages most European chemists understood.

There was an instance during Jannik Bjerrum's lecture which I found amusing. He then spoke in English with great rapidity. He was lecturing in English and was understood perfectly by the Danes and the Germans, but English speakers found it difficult to follow him. At one point in his lecture he wanted to show again the previous slide and said to the operator "Please, the last slide". The operator, being Danish and not understanding English gave him the next slide, at which Jannik Bjerrum got excited and said again "Please, the last slide" and got yet another slide. More excitement and more slides, then a Dane in the audience stood up and told the projectionist in Danish what was needed. Bjerrum then remembered that he could speak Danish and so he started to tell the operator once more what it was he needed. The slides went rapidly back until the correct one was reached, at which point Bjerrum continued his lecture - but in German. Fortunately he didn't get very far. Perhaps the blank expressions on the faces of the large number of English chemists reminded him that his lecture was supposed to be in English.

THE THIRD CONFERENCE

The second conference had again been quite small and the Dutch chemists thought its successor would be a suitable one for their Chemical Society. I thought so too, and since I was then General Secretary I gave them the next date, 1955. They held their conference, the third in the series, from 28th April to 3rd May in that year, with Professor Dr. A.E. Van Arkel as President and Dr. C.L. Van Panthaleon van Eck as Secretary. The conference was now becoming a tradition. The first two conferences had been called symposia. This one was deliberately entitled "The International Conference on Coordination Compounds 1955" and was organised by the Royal Netherlands Chemical Society. I have no record of the number of participants but the number of papers given was 65. The volume of the 'Proceedings' was about twice as thick as that from the Copenhagen conference. It was divided into five sections, each with one or two introductory lectures and a number of contributed papers. My lecture there was on directing effects in inorganic substitution reactions.

The conference was becoming a firm fixture. The 1957 conference had been promised to Italy, the Chemical Society wished to have the 1959 conference in London, and Sweden had asked for the conference in 1961. So far, the meeting had been a small one, mainly organised by small organisations in small countries, but it was growing in size and in reputation. The Rome meeting was the first to be sponsored by the International Union of Pure and Applied Chemistry (IUPAC) and it was also sponsored by the Italian National Research Council and by the Italian Chemical Society. Professor L. Cambi was its President and Professor V. Caglioti its Secretary. There were five sections with plenary lectures and contributed papers, making 78 lectures in all.

THE GROWTH OF THE CONFERENCES

It was at the Rome meeting that things became difficult for me as General Secretary, because now the bigger countries, especially the United States and Germany, wished to hold conferences. Dates had been allocated right through to 1961, with 1965 or 1967 allocated to Switzerland for the Werner Centenary. It had been my place so far, as General Secretary, to allocate dates in order as they were requested and I kept rigorously to that principle, but now the competition to hold the conference was so great that a small *ad hoc* committee was called in Rome by some person unknown to me. It was decided that the General Secretaryship should rotate around the nationalities, but that I should retain it until after the 1959 meeting in London. Sweden, represented by Professor L.G. Sillen, agreed to postpone its conference for a year so that the United States could step into its place in 1961.

This postponement was advantageous in that the regular biennial conferences would cease to fall on odd-numbered years and come on even years as at present: this would avoid conflict with the IUPAC Congress. Stanley Kirschner became local secretary for the U.S. conference in 1961. By this time I was no longer General Secretary, and he dropped into the position. Of course it was impossible for the idea of a rotating Secretaryship to

work since the Secretary was the only link from one conference to the next, and the only man who had records of future conferences. From being local secretary Stanley Kirschner became General, and then Permanent Secretary and the I.C.C.C. conferences since then have gone from strength to strength under his able guidance.

Looking back on those early conferences, I think perhaps the Danish one was the one I enjoyed most. Perhaps because it was my first conference abroad; possibly because Denmark was well provided with food in contrast to England where food rationing had continued until long after the war. Perhaps it was because the English and the Danes have a similar sense of humour. Whatever it was I shall never forget that conference. I hope that I am not hurting anyone's feelings by saying that, because indeed all the conferences on coordination chemistry which I have attended - and I attended every one until the Japanese conference - have been very enjoyable experiences.

The 1959 London conference was held under the auspices of the Chemical Society only, but since then all organisers have requested and received IUPAC sponsorship. The sixth conference was held in Detroit (it was at this point that the conferences began to be numbered). The seventh was in Stockholm and it was at this conference that the ad hoc committee of National Representatives, now well established, decided that because so many invitations were being received for future conferences, they could be held every year. In the even-dated years they would be held in Western Europe or North America, and in the other years in 'faraway places'. The eighth conference was held in Austria in 1964, the ninth in Switzerland in 1966 in commemoration of the Centenary of Werner's birth, the tenth in Japan in 1967, the eleventh in Israel in 1968, the twelfth in Australia in 1969 and the thirteenth in Poland in 1970. 1972 saw the fourteenth conference in Canada; the fifteenth was in the U.S.S.R. in 1973, the sixteenth in Ireland in 1974. Now we have the seventeenth in Hamburg, and it promises to be an excellent conference. Next year will be the turn of Brazil, and after that Czechoslovakia. I have attended all except the tenth, thirteenth, fifteenth, and sixteenth.

SOME OF THE CHEMISTRY

So - we have had some retrospect. What about some chemistry? I had intended to say something about the work on the reactions of ligating dinitrogen which is going on in my laboratory, but I see that Dr. D. Sellmann will be giving a plenary lecture on that subject. I propose instead to say a little about some of the more interesting discoveries in my laboratories, and after that I shall deal with 'prospects'. But, even before that, I would like to tell a story which well illustrates the difference between Italian and English temperament.

I have mentioned that Professor Cambi was the President of the Rome conference in 1957. He was a very impressive man and a great orator, not that I understood what he said because I do not understand Italian and he did not speak English. However, his gesticulations were an art in themselves and wonderful to behold, I used to enjoy hearing and watching him lecture. You all know Professor Luigi Venanzi who, despite his name and birth, is a model English gentleman. At the Rome conference he was there as interpreter to provide an intermittent translation of Professor Cambi's opening address. Professor Cambi gave his address after the manner of great Italian orators, to the accompaniment of dextrous manual expression. After about 10 minutes of marvellous performance, he would sit down and Dr., as he then was, Venanzi would stand up with no more than the flicker of an eyelid in the way of gesticulation and deliver himself of the whole of Professor Cambi's previous 10 minutes in a perfect Oxford English, in just about 1½ minutes flat. 'Professor Cambi has just said ...' Then Professor Cambi would roll on again for another 10 minutes or so, marvellous to behold, to be condensed again into 1½ minutes of translation. Those of you who really want to know what Professor Cambi said can read it all in the Proceedings of the 1957 Conference, but unless you are Italian you can never appreciate him as an orator the way I have, even though I did not understand what he said.

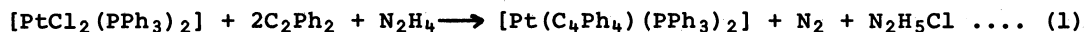
I think I might interest you by saying a little about the nature of scientific discoveries. In the course of a lifetime one can make a great number of interesting and sometimes unexpected discoveries. Very hard

work precedes some of them, others come almost by accident. The electronic structure of olefin complexes, which I have already mentioned as being bound up with the beginnings of the I.C.C.C., was done in the textbook manner. Being a beginner in the art of research I naturally followed the textbook. I made a hypothesis as to the structure, devised experiments to test out that hypothesis, and if my results agreed with what I expected the hypothesis was strengthened, and if it did not the hypothesis was changed. The really important step was the appreciation that 'back bonding' was the important factor. I think you probably know that this arose from my comparison of the complete lack of interaction between ethylene and trimethylborane, even at their freezing points, as compared with the stable complexes formed by ethylene with transition metals in low oxidation states and with closed shell configurations (Ref. 1).

Many great discoveries are purely accidental, and it is surprising how often accidental discoveries are made almost simultaneously and independently in laboratories which are thousands of miles apart. The discovery of ferrocene in 1951 was one such. Two groups of workers, Kealy and Pauson (4) at Duquesne University in Pennsylvania, and Miller, Tebboth and Tremaine (5) of the British Oxygen Company in England simultaneously discovered that substance accidentally. They made it in different ways, and both groups formulated it as analogous to diphenyl zinc. As organic chemists they had forgotten to satisfy the coordination requirement of the ferrous ion. It was immediately obvious to transition metal chemists that they had found a new class of substances which I described then as "extended olefin complexes" because all the carbon atoms of the five membered ring were obviously equally bonded to the metal, as are the two carbon atoms of ethylene in its complexes. Thus started a new vast area of chemistry which has kept two famous chemists working for most of their lives, earned them Nobel Prizes, and gives me a cue to tell you a rather trivial story about my first meeting with one of them.

My first meeting with Professor E.O. Fischer occurred just after he had discovered dibenzene complexes. He came to see me in the Akers Research Laboratories of Imperial Chemical Industries (I.C.I.) Limited which were situated in a country area outside London. Transport was by train to Welwyn Garden City station and by Company car to the laboratory. Our laboratory had two cars and chauffeurs. One was sent to meet Fischer's train but when he was due to arrive in my office I received a phone message, from the I.C.I. Plastics Division Laboratories in Welwyn Garden City, to say that Professor Fischer had telephoned from the railway station asking how to find his way to my laboratory, that he was in a telephone box of a certain number, and I should telephone him there. They had told him to stay in the box until I telephoned. I then telephoned our office to find out why the car had not gone and was told that it had gone. I told them to send the second car which they said they would do, then I telephoned Professor Fischer and because my secretary was German-born I asked her to speak to him. He tells me it was a great relief to find someone whom he could understand easily. We had just ceased this operation when the first chauffeur came to my office to report that my visitor had not arrived. I told him that the visitor had arrived and asked him why he had not telephoned me from the station, to which he replied "I would Sir but I couldn't. There was a foreign looking gentleman in the telephone box and he wouldn't come out". In the end, Fischer and I had a great day discussing benzene and olefin complexes.

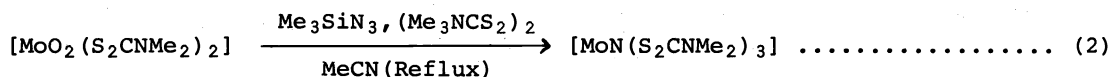
Good discoveries, such as sandwich compounds, are often made by accident. The discovery of trans-[PtClH(PET₃)₂] was one such discovery in my own laboratory (Ref. 6). This was the first transition metal hydride complex which did not contain carbon as a ligand atom. It was discovered as the result of my only attempt to enter the field of sandwich compounds. If one extrapolates from dibenzenechromium through bis-(cyclopentadienyl) iron one arrives at bis(cyclobutadiene)nickel (Ref. 7). Dr. Leslie Orgel exhorted me to try to make a cyclobutadienyl compound. A possible compound was [Pt(C₄Ph₄)(PPh₃)₂], by reaction (1).



However our product was [Pt(C₂Ph₂)(PPh₃)₂], and Dr. G.A. Rowe who did these experiments obtained a great number of analogues from other acetylenes (Ref. 8, never published in full). When we attempted to obtain analogues

from other phosphines, e.g. $[\text{Pt}(\text{C}_2\text{Ph}_2)(\text{PEt}_3)_2]$ from triethylphosphine, we obtained only an oil. It fell to Dr. B.L. Shaw to attempt to purify that oil. He found that the acetylene had no part in the production of this oil. First we thought we had the compound $[\text{Pt}(\text{PEt}_3)_2]$, and because the mononuclear metal(0) compounds then known were mostly volatile we attempted to distil our oil in high vacuum. It distilled as a low melting solid onto a cold finger. Thus we obtained a white solid which, eventually, we formulated as trans- $[\text{PtClH}(\text{PEt}_3)_2]$. We took a lot of convincing that we had a transition metal hydride complex, especially one of platinum so stable that it could be distilled. Platinum salts are usually so easily reduced to the metal that we never expected to obtain a hydride complex of that formula. One would expect it to split away hydrogen chloride to leave a platinum(0) complex, $[\text{Pt}(\text{PEt}_3)_2]$, isoelectronic with $[\text{AuI}(\text{PEt}_3)]$. However, there it was, and eventually an X-ray structure of the corresponding bromide showed that it was a normal planar platinum(II) complex with a vacant space in trans-position to the bromide ligand, which must accommodate the hydride ion (Ref. 9). It showed hydride behaving as a normal anionic ligand. This chance discovery opened the way to the discovery of a vast new area of hydride complex chemistry and preparation of numerous hydride complexes with tertiary phosphines and such substances as co-ligands (Ref. 10).

I shall give just one recent example of another chance discovery in my own laboratory. This was the discovery of thionitrosyl complexes. We are particularly interested in nitrido-complexes, especially those of molybdenum in connection with our studies of nitrogen fixation. Dr. J.R. Dilworth attempted to prepare them by reaction (2).



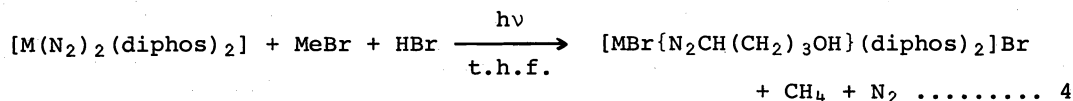
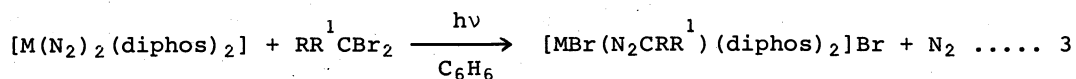
However he obtained a substance which from its carbon and hydrogen analysis appeared to be a nitrito-N-compound $[\text{Mo}(\text{NO}_2)(\text{S}_2\text{CNMe}_2)_3]$. This appeared to be confirmed by the band in the infrared spectrum at 1100 cm^{-1} ; he thought that he had obtained his nitride but that it had oxidised to a nitrito-N-complex. A sulphur analysis quickly showed that the substance contained one atom of sulphur rather than two of oxygen and indeed it is a thionitrosyl complex, the first ever to be recorded. Obviously his nitride was so avid for sulphur that it had extracted it from a sulphur ligand. Of course, the compound is obtained very much more readily by the direct reaction of elemental sulphur with the nitride complex $[\text{MoN}(\text{S}_2\text{CNMe}_2)_3]$ (Ref. 11). I think you might like to see the structure of that complex which has been done by Dr. M.B. Hursthouse and M. Motevalli of Queen Mary College, London, and has not yet been published (Fig. 5). The thionitrosyl complex is closely similar to its nitrosyl analogue (Ref. 12). Surprisingly, the Mo-N distances are not significantly different [1.74(1) and 1.731(8) Å respectively] and the Mo-N-S and Mo-N-O angles are almost identical [$172.1(7)^\circ$ and $173.2(1)^\circ$ respectively].

I could continue with many more examples. How the discovery of alkyl and aryl tertiary phosphine complexes was the result of careful planning where the hypothesis worked and we obtained the stable compounds desired (Ref. 13). How the attempt to discover the distribution of electric charge in complex compounds involved the measurements of great numbers of dipole moments over the whole period of 25 years since these conferences started (Ref. 14), and so on, but there is not time. And now I must go on to prospects.

What have been the main advances in coordination chemistry during the past 25 years? I think it is undoubtedly the vast expansion in our knowledge of organotransition metal chemistry. Twenty-two years ago the whole of this chemistry including olefin complexes was provided by Dr. F.A. Cotton in a detailed review of four pages (Ref. 15). Now it is so vast that even the organic chemistry of one element, palladium, fills a book of 319 pages (Ref. 16), and the chemistry of the olefin, hydride and alkyl complexes lies at the basis of a number of important industrial processes. Another big field of rapid expansion has been in the study of the stabilities of complex compounds in aqueous solution, both of inorganic complexes and quite complicated organic complexes. Following on that has been the study of inorganic reaction mechanisms and the explanation of the trans-effect. Complex chemistry was once largely aqueous chemistry, within the last

quarter century much of it has been brought into non-aqueous media by the use of organic ligands. Tertiary phosphines and arsines were initially used simply for the purpose of rendering complex compounds fusible, or soluble in organic solvents, but such complexes once they had been made in numbers were found to have unique properties quite different from those of the amines and the water soluble complexes which had preceded them. Thus a vast area of non-aqueous complex chemistry has arisen. It is closely interwoven with the development of organotransition metal chemistry and of metal cluster complex chemistry.

We are now seeing the development of the complex chemistry of dinitrogen and this brings me to our present study of the reactions of ligating dinitrogen. The catalytic activation of dinitrogen under ambient conditions is important because dinitrogen is cheap and abundant, but useful nitrogen compounds are at present manufactured from it by indirect methods. The reaction of dinitrogen with transition metal complexes to give dinitrogen complexes and the further reaction of some of these to give ammonia or complexes of organic nitrogen compounds is well established (Ref. 17). Our most recent developments in this field show that complexes of diazomethane and related substances are readily obtained by reactions of the general types 3 (Ref. 18) and 4 (Ref. 19).



(M = Mo or W; R = R¹ = alkyl or H; diphos = Ph₂PCH₂CH₂PPh₂;

t.h.f. = tetrahydrofuran).

Reaction 4 is remarkable in that the hydrocarbon chain and oxygen of the ligating diazobutanol is derived from tetrahydrofuran, presumably by a radical mechanism.

The chemistry of ligating dinitrogen is just opening up and is probably at the same stage of its complex chemistry as was olefin complex chemistry at the time of the second I.C.C.C. in 1953, but there the resemblance ends. In 1953 complex chemistry was unfashionable and olefin complex chemistry a backwater of chemistry, now dinitrogen complexes and their chemistry are really hot stuff.

PROSPECT

What of the future, whether it be of complex chemistry, or of the International Conferences on Coordination Chemistry? I have cribbed a diagram (Fig. 6) from Lord Ashby's 'Second Look at Doom', published in the 'Esso Magazine', Spring 1976. If we may believe his prediction, both our chemistry and the I.C.C.C. will continue to flourish for another 25 years. After that we may see a rapid change in the direction of the fortunes of both chemistry and the I.C.C.C. as the population continues to rise and the world's resources to fall rapidly. So let me limit my predictions to the next 25 years.

Coordination chemists are only just beginning to get interested in metallo-enzymes, these are much too complex to be more than imitated only very crudely by coordination chemists at the present time but as the new spectroscopic methods of structure determination are found, and existing methods become more refined, more will be learnt about the environment and function of the metal atoms. Then inorganic chemists will be able to build genuine models, possibly with unique catalytic properties, based on a precise knowledge of structure. Perhaps the nearest thing we have to this at the present time are the iron-sulphur cubane cluster compounds of R.H. Holm (20) as models for the redox centres present in some non-haem iron proteins.

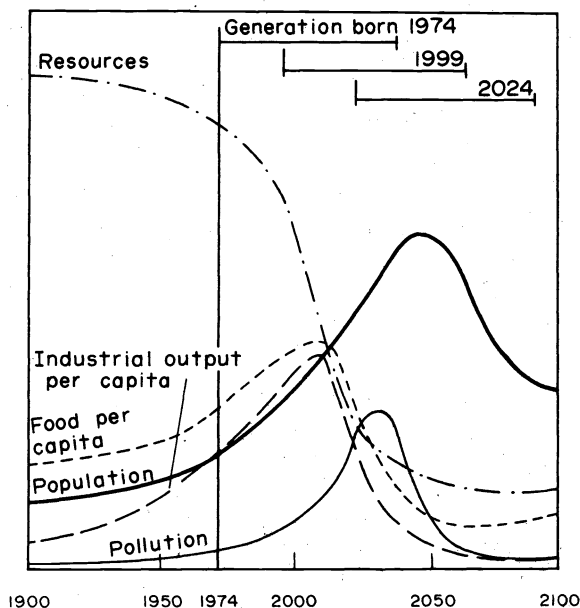
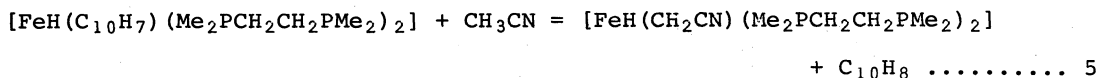


Fig. 6 A computer model incorporating historical trends for factors such as food, population, industrial output and pollution and projecting these forward into the future shows an eventual collapse of population - 'Doom'

There appears to be a vast area of coordination chemistry to be discovered from more precise information about the environment and function of the metal atoms in metalloenzymes, such as was heralded by the discovery of the structure of olefin complexes about 25 years ago.

An area of considerable interest which has hardly been touched is the activation of saturated hydrocarbons by transition metal complexes. The splitting of both aromatic and aliphatic C-H bonds by strongly reduced transition metal centres was discovered in my laboratory in 1965, in a ruthenium complex (Ref. 21), but owing to a change in the direction of my work was never followed up. I have just learnt from S.D. Ittel (22) that he and his co-workers at Du Pont's Experimental Station in Wilmington have made iron analogues of our ruthenium compound. These react very readily with organic substances, such as methyl cyanide, which contain slightly activated hydrogen by splitting the C-H bond according to reaction 5.



Quite obviously there is a new area of complex chemistry involved in the splitting of saturated C-H bonds, and I think it is probably in the stage that olefin complex chemistry was in about 1930.

The energy crisis has forced upon chemists' attention the need to develop methods of receiving and storing the sun's energy. Can the coordination chemist help? Perhaps he can. You may have noticed recently that Professor D.G. Whitten and co-workers of the University of North Carolina have shown that the complexes of the type $[\text{Ru}(\text{dpy})_3]^{2+}$ (dpy = 2,2'-dipyridyl) under certain conditions cause the photo decomposition of water into hydrogen and oxygen, which could in turn be a source of high grade energy (Ref. 23). How far is it possible to expand and improve such processes? If there is any promise here, there will be a great expansion in the study of the photochemistry of complex compounds.

I have mentioned just a few areas which I can see starting to develop at the present time, but of course all the main areas of complex chemistry which are going so strongly at present are by no means exhausted. The chemistry of the later transition metals has opened up tremendously during the past 25 years, but the complex chemistry of the early transition metals is only just beginning. Spectroscopic and structural methods have just

now reached the degree of sophistication necessary for the real development of that area of complex chemistry. It will undoubtedly develop because compounds of those metals have shown themselves to be unique in the reactions of their dinitrogen complexes, and in the olefin dismutation reaction. Many other catalytic reactions may unfold from the study of early transition metals.

The large cloud on the horizon is that represented by Lord Ashby's prophecy of doom, but it is not the first time doom has been forecast and it has been side-stepped by the application of new scientific discoveries. I do not see why it should not be so again if population growth can be curbed. Food is the first essential and that is one reason why I find myself now interested in one of the problems of the Agricultural Research Council.

It is interesting to look at past predictions. I have a chemistry textbook written in the 1840's whose author saw the vast expansion of the railways and predicted the disappearance of the main roads and Coaching Inns. He foresaw the future with railways linking together the towns and villages and a small local road system used to distribute by horse and cart the goods which were delivered at railway stations. For half a century he was almost right. The long distance horse traffic disappeared, Coaching Inns ceased to flourish and the road system atrophied. But look at it all now. The road system is growing and the railways atrophied. It is always dangerous to predict the future, but I think that over the next 25 years the main new development in inorganic chemistry will be its reaching out into the realms of biochemistry and the increase of our understanding of the role of metal ions in life's processes.

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