

CO-ORDINATION CHEMISTRY

THE Fourth International Conference on Coordination Chemistry was organized by the Chemical Society and held in London under the sponsorship of the International Union of Pure and Applied Chemistry during April 6-11. Since 141 contributions were received (from twenty-three different countries) in addition to seven invited lectures, it proved necessary to hold three concurrent sessions for the reading of papers. The following report is therefore necessarily based on direct attendance at only a sample of the papers presented and otherwise on the preprinted abstracts.

Prof. K. Ziegler (Mühlheim) in the first of the general lectures began by giving an account of the various steps involved in the catalytic polymerization of olefins by aluminium alkyls and concluded with some remarks on the influence of titanium salts on this reaction. The latter topic was taken up in a paper by G. Natta and G. Mazzanti (Milan), who presented evidence on the structures of some mixed complexes of titanium and aluminium which may be involved. The mechanism of the reaction between aluminium alkyls and titanium halides was further discussed in a paper from Israel.

Dr. H. M. N. H. Irving (Oxford) reviewed the available information on the stability of metal complexes in solution and showed how some simple theoretical ideas could be used to establish useful correlations. Among the many interesting contributions on this topic one may mention a study of thio-complexes from G. Schwarzenbach's laboratory in Zürich, a paper on the heats of formation of ethylenediamine complexes by M. Campolini and co-workers (Palermo), a study of polynuclear copper (II) complexes of carboxylic acids by D. L. Martin and F. J. C. Rossotti (Edinburgh) and work on silver (I)-oxine complexes by D. Dyrssen and co-laborators (Stockholm).

Prof. H. Taube (Chicago) reviewed recent work on the mechanisms of complex ion reactions in solution and described some entirely novel experiments of his own. He provided conclusive proof that during the course of the oxidation-reduction reaction between cobalt (III) and chromium (II) ions under appropriate conditions, electrons are transferred through the whole length of the terephthalic acid molecule, and further showed that if the methyl ester of terephthalic acid was present, it was hydrolysed in the course of the reaction. This work opens the way for a full-scale attack on the vexed problem of electron transport through conjugated systems, and should have important consequences.

Studies on the mechanisms of the photochemical reactions of complex ions were reported by S. T. Spees and A. W. Adamson (University of Southern California), who discussed the possible role of doublet states in the photochemistry of chromic complexes; another paper on this subject was given by D. R. Stranks and G. J. Weston (Leeds). Contributions on the detailed kinetics of the hydrolysis of chromic complexes were presented by J. Bjerrum and co-workers (Copenhagen), who infer the existence of the $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})]^{4+}$ ion as an intermediate in the hydrolysis of $[\text{Cr}(\text{en})_3]^{3+}$, and by H. L. Schläfer (Frankfurt am Main), who studied the equation of $[\text{CrO}_2(\text{OH})]^-$.

Dr. Greenberg presented the results of some recent studies from the U.S.S.R. on the *trans* effect in the substitution reactions of platinum (II) which suggest that the experimental situation is more complicated than has been previously realized. The first studies of the kinetics of the substitution reactions of *bis*cyclopentadienyl titanium dihalides were reported by A. Jensen and F. Basolo (Northwestern University, Illinois). The exchange reaction of quadridentate complexes, particularly of nickel (II), were discussed by W. W. Fee and B. O. West (Adelaide), and the kinetics of the dissociation of complex cyanides and of ethylene-diamine nickel complexes by G. Emschwiler (Paris) and by A. K. Shamsuddin Ahmed and R. G. Wilkins (Sheffield), respectively.

Some of the liveliest discussions followed papers of a rather theoretical nature dealing with the spectra and magnetic properties of complexes, for example, a paper on the relation between the geometrical structure and the magnetic properties of nickel (II) complexes by G. Maki, and another on the effect of the thiocyanate ion on the spectra of metal ions by C. E. Schäffer (Copenhagen). An interesting account of the magnetic susceptibility of rhenium compounds was given by B. Jezowska-Trzebiatowska (Wrocław). The variation of the magnetic susceptibility of vanadium (III) complexes with temperature was discussed by B. Figgis, J. Lewis and F. E. Mabbs (University College, London). Two papers, one by S. Minc and W. Libus (Warsaw) and the other by F. A. Cotton and R. H. Holm (Massachusetts Institute of Technology), dealt with the physical properties and relative stabilities of the various types of cobalt (II) complex which exist in solution, and two others, one by C. R. C. Coussmaker and collaborators (Oxford) and the other by A. Turco and G. Giacometti (Padua), considered the properties of the versatile complexes of nickel (II) with substituted phosphines.

The X-ray determination of the structure of a complex formed by azobenzene and arsenic trichloride was reported by E. Ferroni and P. Orioli (Florence); the cuprous-diazoaminobenzene complex was shown by I. D. Brown and J. D. Dunitz (Royal Institution, London) to be dimeric in the crystal and to involve an eight-membered ring containing six nitrogen and two copper atoms. M. R. Truter and her co-workers (Leeds) discussed the structure of β -diketo complexes of trimethyl platinum (IV). Other structures described included those of basic zirconium chromates and β - $\text{Zn}(\text{OH})\text{Cl}$. An important paper by I. Linqvist (Uppsala) surveyed the structures of some addition compounds of phosphorus oxychloride and selenium oxychloride.

A further group of contributions dealt with the elucidation of molecular and electronic structure by means of infra-red and Raman spectroscopy. K. Nakamoto, P. J. McCarthy and A. E. Martell (Clark University, Worcester, Mass.) discussed the infra-red spectra of the metal complexes of β -diketones, while D. B. Powell and N. Sheppard (Cambridge) dealt with the metal complexes of amines and ethylenediamine and showed that for the latter both *cis* and *gauche* configurations of the ligand are possible. Infra-red spectra of heteropolytungstates

were reported by a group of workers from Moscow. Raman spectra of addition compounds of sulphur trioxide were reported from Amsterdam and of stannic chloride from Karlsruhe.

Among the many papers principally concerned with the preparation of new compounds and the elucidation of their reactions one can pick out only a few. S. Herzog and co-workers (Jena) described the extension of their work on dipyriddy complexes of metals in abnormally low valencies to the preparation of the diamagnetic $[\text{Ti}(\text{dipyridyl})_2]^-$ ion; L. Naldini (Milan) described a series of salts of the low-spin (hexa-aryl isocyanide)-manganese (II) complexes; V. Cagliotti and co-workers (Rome) discussed the preparation and reduction of the oxygen adducts of cobalt (II)-histidine complexes.

Carbonyls of iridium (III), isocyanides of rhodium (II) and phosphines of osmium (I) were reported by L. Malatesta and S. Sandroni (Milan), by Miss L. M. Vallarino (Milan) and by L. Vaska (Mellon Institute, Pittsburgh), respectively. Complex fluorides of molybdenum and tungsten and rhenium were discussed by G. B. Hargreaves and R. D. Peacock (Birmingham); R. Hoppe and co-workers (Münster) reported on a variety of zirconium, tin and manganese complex fluorides. Heteropolyacids and related polyanionic compounds were treated extensively by groups from Roumania, the U.S.S.R. and Sweden. The properties of volatile nitrate-iron complexes and copper perchlorates were described by C. C. Addison and N. Logan (Nottingham) and by B. J. Hathaway (Hull), respectively.

The subject most completely covered both in general lectures and contributed papers was that of organo-metallic compounds involving transition metals. Dr. E. O. Fischer (Munich) surveyed experimental work on compounds involving 'sandwich' bonding in a comprehensive and lucid fashion. Prof. R. Nast (Heidelberg) described in detail his important researches on the complex acetylides of the metals; the least stable it appears are spontaneously explosive and the more stable only pyrophoric. Dr. H. W. Sternberg (Pittsburgh) discussed recent experimental work on the reactions of acetylenes, etc., with metal carbonyls and produced some interesting speculations on the relevance of these results to problems both of homogeneous and heterogeneous catalysis. Dr. L. E. Orgel (Cambridge) discussed bonding in zero-valent metal compounds.

Determinations of the crystal structure of some organo-transition metal complexes were reported by A. A. Hock, O. S. Mills and G. Robinson (Manchester); the results were, as usual in this field, very surprising. The infra-red spectrum of chromium dibenzene was described by A. Fritz (Munich). The symmetry of this molecule was discussed at some length. The view of the German school was that theory predicted it to have only three-fold symmetry as argued by E. Ruch (Munich) in a contributed paper. A number of other theoretical chemists (the present author included) held that no definite prediction could be made, but strongly favoured the view that the symmetry would prove to be six-fold. The experimental evidence, it seems, is not yet unambiguous.

A paper by L. S. Meriwether, Marilyn Fiene and G. W. Kennerly established that substitution reactions of a number of nickel carbonyl-phosphine complexes occur by way of a three co-ordinated intermediate rather than by a second-order mechanism. The reactions accompanying the polarographic reduction of iron carbonyls were considered

by A. A. Vlček (Prague). There was some discussion of a paper by D. A. Brown (Queen Mary College, London) on the effect of phenyl-substitution on the stability of sandwich compounds.

The preparative work described in the field of acetylene-carbon monoxide chemistry was varied, fascinating, and still largely incomprehensible. G. Natta and co-workers (Milan) discussed the synthesis of succinic acid from carbon monoxide, acetylene and water in the presence of metal carbonyls. They suggested that it required binuclear metal complexes as intermediates and provided good evidence for the occurrence of a peculiar lactone-like derivative of succinic acid as a ligand in certain metal complexes. W. Hübel and E. H. Braye (Brussels) described the numerous new compounds which they have prepared from iron dodecacarbonyl and acetylenes. Some compounds contain aromatic rings, some contain cyclopentadienone, and others cannot at present be formulated in an acceptable fashion (like $\text{C}_2\text{H}_2\text{Fe}_2(\text{CO})_6\text{H}_2$, they probably do not have 'acceptable' structures). E. Weiss and W. Hübel described the reactions of cyclopentadienones with metal carbonyls. They demonstrated the ability of cyclopentadienone in certain sandwich compounds to behave more like the anion derived from a phenol than like a normal ketone. Presumably this is due to charge-transfer from the metal to the oxygen of the ring.

The insertion of carbon monoxide into organic molecules by way of metal carbonyls was part of the theme of some of the general lectures. It was discussed in detail for the case of alkyl and acyl manganese carbonyls by T. H. Coffield and co-workers (Ethyl Corporation Laboratories, Detroit), who described some carbon monoxide exchange studies which throw considerable light on the reaction mechanisms involved. L. Kirch and M. Orchin (Cincinnati) described recent experimental work on the oxo-reaction.

Contributions on other metal alkyls included a discussion of the reactivity of the cadmium compounds by J. Vène (Rennes), a paper on alkyl and aryl palladium compounds by G. Calvin, G. E. Coates and P. S. Dixon (Durham), and another on the determination of Grignard reagents by F. G. Mann and I. T. Millar (Cambridge).

A group of papers described catalytic reactions other than those in the carbonyl field. One may mention that of W. Brackman (Royal Dutch Shell, Amsterdam), who described a series of copper-amine complexes which catalyse the oxidation of alcohols, and that of M. T. Beck (Szeged), who described much interesting work on catalysis that has been carried out in Hungary.

Of the papers not directly concerned with metal chemistry I shall mention one, the presidential address of the Chemical Society, which was open to all members of the Congress. Prof. H. J. Emeléus outlined the experimental situation in the field of inorganic polymeric molecules and amply illustrated his thesis that this is a fascinating and largely unexplored region of inorganic chemistry.

The Conference, seen as a whole, left one with no doubt that co-ordination chemistry has entered a period of rapid growth and is already invading fields which traditionally were distinct from it. The development of the various syntheses of large conjugated molecules from carbon monoxide and acetylene can scarcely fail to influence organic chemistry. The close contact between ligand field

theory and experiment in the field of co-ordination chemistry provides, perhaps for the first time, a climate in which experiments are designed to test the quantitative predictions of electronic theory; this must prove beneficial to both.

The organization of the Conference, both of the scientific meetings and the more social occasions, was

uniformly excellent. All those who were present must be grateful to the members of the Chemical Society committees who were responsible for it and to those industrial concerns which, by their financial support or by acting as hosts, helped to make the meeting so successful.

L. E. ORGEL

THE BRITISH COAL UTILIZATION RESEARCH ASSOCIATION

TWENTY-FIRST ANNIVERSARY OPEN DAYS

THE aim of the Association, from the time of its inception in 1938, has been "to promote research and other scientific work in connexion with the utilization of coal and its derivatives". Some of the achievements of twenty-one years were displayed at the research station during April 22-24.

In 1938, nine experimentalists worked in a single room, 12 ft. square, in Victoria Street, London. To-day the British Coal Utilization Research Association occupies a 20-acre site at Leatherhead, and is one of the largest of the thirty-nine industrial research associations supported by the Department of Scientific and Industrial Research; of its total staff of some 300, eighty are graduates or equivalent and a similar number are research assistants, representative of most of the recognized fields of physical science, from mathematics through the several branches of chemistry and physics to large-scale engineering.

The interests of the Association are many-sided, and this was reflected in the distinctive character of each of the three open days. April 22 was primarily 'members' day; through its membership the Association forms a link between the four nationalized industries (coal, gas, electricity, transport) and about 150 other members (comprising individual firms and trade associations) which include industrial appliance makers, coal distributors and coal consumers. The Minister of Power, the Right Hon. Lord Mills, was the guest of honour, and in addressing a large and distinguished gathering at luncheon, he observed that the occasion marked the coming-of-age of an Association which had long since established itself as one of the most important and progressive industrial research organizations in Britain.

On the second day the guests were mainly drawn from the field of research; Government departments, research associations, universities and technical colleges were strongly represented. On the morning of the final day parties from local colleges and schools predominated, thus emphasizing the practical interest taken by the British Coal Utilization Research Association in educating young people in the science and technology of coal. In the afternoon the Association was honoured by a visit of a party from the London Section of the Royal Institute of Chemistry; and the day was fittingly concluded by a lecture to this party and other chemists by Prof. R. G. W. Norrish on recent work at Cambridge on flash photolysis in gases.

Throughout its history the British Coal Utilization Research Association has been in close touch with university thought and investigation and has itself maintained a strong programme of basic research. One well-known example of the effectiveness of this approach is the outcome of the experiments on coal breakage which were started in that small over-

crowded laboratory in London in 1938. After some years of investigation, in collaboration with the British Colliery Owners Research Association, a specification for grading coal by size was drawn up, and this has been accepted by the National Coal Board as a basis for preparing and marketing coal. Another example of the application of basic research, also exhibited in the Physics Department, was the cone mill. Following a survey of the factors determining the power required for grinding coal to a given size, determination of the Hardgrove grindability index, and measurement of the intrinsic physical and mechanical properties of coal, a matrix theory of coal breakage was developed and the first cone mill was built to test this theory: now its engineering utility is being studied.

Some of the modern techniques being used to investigate both the chemical and the physical aspects of coal constitution were displayed. Research into the chemical basis of the plastic softening of coals, with the view of achieving better control of coking properties, has recently made considerable progress, and current knowledge of the mechanism was illustrated diagrammatically alongside the special apparatus employed. Another exhibit was of interest as the first complete conversion, in a single step, of coal to chemical products without simultaneous production of tar or solid residue: low-rank coals have been treated with chlorine trifluoride, producing a range of chlorofluorocarbons (from colourless oils to resin-like solids) possessing chemical and physical properties that indicate their possible suitability for certain industrial applications.

Considerable work by the Association over a number of years on the ultra-fine porous structure of coal and its development during carbonization has led to the placing, by the U.K. Atomic Energy Authority, of a research contract for fundamental work on the graphite used as moderator in nuclear reactors. This investigation has already shown that closed pores in the graphite become accessible during its reaction with oxidizing gases, and an estimate of the importance of internal burning has been obtained.

Among the current major problems facing the coal industry are: improvement of methods for using small coal; meeting the challenge of competition from oil; and assistance in the implementation of the Clean Air Act. Research by the Association has, therefore, been directed especially towards: (a) improving and devising appliances suitable for burning small coal; (b) developing methods for the automatic control of combustion; and (c) investigations on reduction of atmospheric pollution from coal-burning appliances.

One of the most important current needs is a method of converting small coal cheaply to gas, and ultimately