

Co-ordination Chemistry of the Platinum Metals

Under the sponsorship of the International Union of Pure and Applied Chemistry, an International Conference on Co-ordination Chemistry was held in London from April 6th to the 11th. The very great interest in the chemistry of the platinum group metals was clearly demonstrated by the number of papers submitted to the Conference dealing with the co-ordination chemistry of this group of elements.

The great interest in the co-ordination chemistry of the platinum group metals is prompted by several factors. Among these are the realisation that the chemistry of these elements is ill-understood, while the formulation of even well-known compounds is now accepted to be far less simple than had previously been appreciated. Thus a paper by Fletcher, Woodhead, Greenfield, Gill and Hardy produced evidence to show that certain chloro-complexes of ruthenium, such as that of empirical formula $\text{Ru}(\text{OH})\text{Cl}_3$, which have always been assumed to be mononuclear derivatives of ruthenium (IV), should be reformulated in terms of polynuclear species. These authors also studied the properties of the ruthenium ammino complex known as ruthenium red, the formulation of which has always been in dispute, with a view to elucidating its structure. They concluded that the intense colour is attributable to a polynuclear diamagnetic cation containing three ruthenium atoms joined by amino- and hydroxo-bridges, a structure analogous to certain cobalt complexes.

Earwicker, in addition to describing some hitherto unknown sulphito-complexes of palladium (II), discussed the structure of such complexes and brought into question the existence of the anion $[\text{Pd}(\text{SO}_3)_2]^{2-}$ suggesting that in solution it was more probably $[(\text{H}_2\text{O})_2\text{Pd}(\text{SO}_3)_2]^{2-}$. He tentatively suggested that in the anhydrous solid the anion is polynuclear, each sulphito-group joining two palladium atoms, one strongly through

sulphur and the other weakly through oxygen.

The wide range of valency exhibited by platinum group metals offers a field of study for the chemist interested in unusual valency states. Bivalent rhodium complexes prepared by reacting rhodium (III) chloride with phenylisocyanide in the presence of sodium iodide were described by Vallarino. The parent compound is formulated $[\text{Rh}_2\text{I}_2(\text{CNPh})_8]\text{I}_2$ and this reacts in chloroform or similar solvents to give $[\text{Rh}_2\text{I}_3(\text{CNPh})_7]\text{I}$. She also reported, in a further paper, rhodium having the oxidation number +I in two series of anions, viz: $[\text{RhX}_2(\text{CO})_2]^-$, (X=Cl, Br, I) and $[\text{Rh}_2\text{X}_4(\text{CO})_2]^{2-}$, (X=Br, I), which were isolated as tetraphenylarsonium and substituted ammonium salts.

Lever and Powell reported the isolation of ammino complexes of bivalent ruthenium, the parent compound being hexamminoruthenium dichloride, $[(\text{NH}_3)_6\text{Ru}]\text{Cl}_2$. They described the reactions of this compound, stressing its powerful reducing properties. In the course of the study of these reactions hitherto unreported amines of trivalent ruthenium had been identified and indications obtained, as in the reaction with sodium chloroaurate in which the final product under controlled conditions was octovalent ruthenium as the tetroxide, of amines of ruthenium in a valency state greater than three.

Vaska reported and described the properties of a series of uni-, bi-, ter- and quadri-valent osmium complexes with triphenylphosphine

and triphenylarsine. The hitherto unknown univalent osmium is represented by $[\text{Os}(\text{Ph}_3\text{P})_3\text{Cl}]$, $[\text{Os}(\text{Ph}_3\text{P})_3\text{Br}]$, $[\text{Os}(\text{Ph}_3\text{As})_3\text{Cl}]$, and $[\text{Os}(\text{Ph}_3\text{As})_3\text{Br}]$. In addition, he reported an apparently zerovalent osmium compound $[\text{Os}(\text{Ph}_3\text{P})_3]$.

Interest in carbonyl complexes of the platinum group metals was illustrated by two contributions referring to carbonyl complexes of iridium. Angoletta reported upon the reaction of $\text{K}_3[\text{Ir}_2(\text{CO})_2\text{Cl}_5]$ and its bromine analogue with aliphatic and aromatic amines. Compounds of the type $[\text{IrX}(\text{CO})_2(\text{amine})]$ ($\text{X} = \text{Cl}$ or Br) were formed and these reacted with triarylphosphines to give $\text{IrX}(\text{CO})(\text{Ar}_3\text{P})_2$ and with triarylsarines to give both $\text{IrX}(\text{CO})_2(\text{Ar}_3\text{As})_2$ and $\text{IrX}(\text{CO})(\text{Ar}_3\text{As})_2$. Malatesta and Sandroni have found that by reaction of a mixture of iridium triiodide and alkali iodide with carbon monoxide at high pressure iodocarbonyliridates of a new type are formed. $\text{K}[\text{Ir}(\text{CO})_2\text{I}_4]$ and $\text{K}_2[\text{Ir}(\text{CO})\text{I}_5]$ were isolated from reactions carried out at 80 to 250°C, but at higher temperatures $\text{K}_2[\text{IrI}_5]$, a new complex, was formed. Three types of iodocarbonyliridium compounds were formed in the reaction between carbon monoxide and iridium triiodide, namely $\text{Ir}(\text{CO})_2\text{I}_3$, $\text{Ir}(\text{CO})_3\text{I}_3$ and the known $\text{Ir}(\text{CO})_3\text{I}$.

Organo - Metallic Compounds

There is a widespread interest in compounds with metal-to-carbon bonds, such as metal-alkyl and metal-aryl compounds, having sigma bonds. Equally, there is also intensive investigation at the present time of metal complexes of olefines and unsaturated ligands generally, and the platinum group metals are some of the few which form bonds with, for example, ethylene. In compounds of these types, particularly in those of platinum and palladium, unusual stereochemistry is often found and problems associated with configuration are being vigorously studied.

These interests were well exemplified by several papers submitted to the Conference. Hellman, Babushkin and Gribov reported a

detailed analysis of infra-red spectra of complex compounds of platinum with ethylene and propene such as $\text{K}[\text{C}_2\text{H}_4\text{PtCl}_3] \cdot \text{H}_2\text{O}$ and $\text{K}[\text{C}_3\text{H}_4\text{PtCl}_3] \cdot \text{H}_2\text{O}$ and outlined their conclusions regarding the bond characters of the central atom and of the unsaturated molecules. X-ray analysis of $\text{trans}-[\text{C}_2\text{H}_4\text{HN}(\text{CH}_3)_2\text{PtCl}_2]$ and $\text{trans}-[\{(\text{C}_2\text{H}_5)_3\text{P}\}\text{PtHBr}]$ was used by Owston to determine the bond lengths in the complexes and so elucidate their structure.

Platinum complexes derived from acetylenes have been isolated by Chatt and Rowe who reacted platinumous complexes of the type $\text{cis}-[(\text{RR}'\text{R}''\text{P})_2\text{PtCl}_2]$ (R , R' , $\text{R}'' =$ alkyl or aryl groups) with acetylenic hydrocarbons in alcoholic medium in the presence of hydrazine hydrate. The halogen was replaced by the acetylene, or a closely related hydrocarbon radical, the type of product depending upon the substituent groups in the phosphine. When the phosphine was purely aliphatic the complexes derived from phenylacetylene were either acetylides, e.g., $[(\text{Pr}^n\text{P})_2\text{Pt}(\text{C}\equiv\text{CPh})_2]$ or styryl derivatives, e.g., $[(\text{Pr}^n\text{P})_2\text{Pt}(\text{CH}=\text{CHPh})_2]$. When the phosphine was purely aromatic the acetylenic substances formed complexes exemplified by $[(\text{Ph}_3\text{P})_2\text{PtCH}\equiv\text{CPh}]$. Mixed alkyl-aryl phosphines gave complexes similar to these three types and no other types.

Calvin, Coates and Dixon described some alkyl and aryl derivatives of palladium, generally with tertiary phosphine ligands. They concluded that the palladium complexes are less stable than the platinum analogues. The complexes $[\text{Me}_3\text{P}]_2\text{PtCl}_2$, $[\text{Me}_2(\text{CF}_3)\text{P}]_2\text{PtCl}_2$, and $[\text{Me}(\text{CF}_3)_2\text{P}]_2\text{PtCl}_2$ were isolated and identified by Beg and Clark in work done on complex formation by phosphines containing the trifluoromethyl group. The order of stability was determined and related to the effect of the more electronegative trifluoromethyl group on the donor properties of the phosphorus atom and hence on the relative strengths of the sigma- and pi-bonds between phosphorus and platinum.

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