A SYMPOSIUM ON COMPLEX INORGANIC COMPOUNDS[1]

INTRODUCTION TO THE SYMPOSIUM

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No apology need be made for a more extended study and discussion of the subject of complex inorganic compounds. In fact, it would be difficult to define such an all-inclusive term as "complex compound," for the simple reason that the formation of complexes is an inherent feature of many chemical reactions. The assumption is prevalent among many chemists that the compounds so designated are the well-known cobalt, chromium, and platinum ammines first studied in detail by Werner and his students. It should be evident from the titles listed for discussion at this symposium that the Werner complexes represent only a special division of an exceedingly diverse and extended class of substances.

Actually there is little difference, except one of degree, between the well-known Werner complexes of cobalt, chromium, and platinum, and many other ammines (ammonates), hydrates, and the great number of organic and inorganic molecular addition compounds. It makes little difference whether the coördinating atom is metallic or non-metallic in character, or whether the coördinated constituent is an atom, ion, or molecule. The same sort of bonding characterizes ammines, hydrates, and other solvates. It is also the distinguishing characteristic of the linkages in the iso- and hetero-poly acids, and the amphoteric oxides, amides, sulfides, and cyanides. The covalent link accounts for the formation of many complex minerals. The argon–boron trifluoride compounds recently discovered by Booth and his coworkers owe their existence to the fact that the argon atom may donate a pair of electrons to boron.

Recent developments in theoretical chemistry and in research technique have given new prominence to this field. The Brönsted concept of acid–base equilibria has directed attention to complex ions in the development of acidic and basic properties in solution, while the ever-changing theories

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of atomic structure have demanded investigation of the physical and chemical properties of compounds characterized by the covalent link. The modern interest in theories of optical activity has stimulated careful investigation of the optical properties of both organic and inorganic substances. At the same time, improved apparatus and the development of new research techniques, such as are furnished by x-ray and electron diffraction methods, have made it possible to gain new knowledge of the structure of all types of compounds.

From a purely practical point of view there is every reason for a more detailed study of complex inorganic compounds. We need think only of the applications and the uses of complex compounds in analytical chemistry in the qualitative detection and quantitative estimation of many cations and anions, and as indicators. Complex cyanides are formed in the separation of precious metals from their ores and are used in the electrodeposition of many metals. The organic chemist has long used various poly acids for the precipitation of certain alkaloids. Attention has also been directed to the use of complex compounds as specific reagents for the isolation of certain amino acids.

The opportunities for investigational work in this field seem to be unlimited. The formation of complex, or "solvated" ions should most certainly be considered in any theory of electrolytic solution which is proposed. Unfortunately, chemical interaction of solvent with solute is tacitly disregarded in most of our modern theories. The number of complex compounds which have been studied by x-ray methods is relatively small. This valuable tool of research should be pressed into service for the determination of the structures of many more of these substances. It should be pointed out that altogether too little is known concerning the stability relationships among complex compounds. A general theory of amphoterism as applied to amphoteric oxides, amides, sulfides, cyanides, etc., is in need of elucidation. Formation of large molecular aggregates or complexes in a further study of colloidal behavior would seem important. Methods of preparation of many of the complex inorganic compounds are largely empirical. Here the synthetic inorganic chemist has a field of endeavor which should warrant his utmost efforts. As a tool for research complex compounds offer innumerable possibilities in the study of configuration, isomerism, and the mechanism of optical activity.

In considering papers for presentation at this symposium the chairman suffered from an embarrassment of riches. The subjects chosen for discussion indicate the varied character of the investigational possibilities in the field of complex inorganic compounds. It is to be hoped that subsequent symposia will give opportunity for discussion of other phases of this extremely interesting subject.

To Professor Rodebush (and W. M. Latimer) must be given the credit for first pointing out the possibility of coördination through the hydrogen bond. In his paper on the hydrogen bond and coördination Professor Rodebush cites many examples of hydrogen bonding in accounting for such interesting phenomena as association of molecules in the liquid state and anion solvation. A new theory for the behavior of the unusual solutions of the alkali and alkaline earth metals in liquid ammonia is also presented.

Professor Bailar has been singularly successful in applying the methods of the organic chemist to the study of isomeric relationships among the cobalt complexes. The Walden inversion, so common in organic chemistry, finds its counterpart in the case of the optically active inorganic complexes. The possibility of employing optically active Werner complexes in the resolution of organic compounds is also an interesting feature of the paper by Professor Bailar.

Recent concepts of solvolysis and solvation, and the behavior of complex ions as acids and bases are reviewed by Professor Hall. The earlier experimental findings of Werner, Lamb, and others are interpreted in terms of our modern theories. It is significant in this connection that much of Werner's work on his own oxonium theory fits in very nicely with our present views.

The polyhalides have always puzzled the theoretical chemist. Their relationship to certain parent solvents is discussed by Professor Booth,[2] who has greatly extended this class of compounds by preparing a whole series of polyhalides containing fluorine.

[2] The fifth paper in this symposium, entitled "The Polyhalides" and presented by Harold Simmons Booth of Western Reserve University, was received too late for publication in this issue, but will appear in a subsequent number.—Editor.