Editorial Note

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Editorial Note on Cluster Chemistry

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Cluster chemistry is one of the recent, exciting areas of Inorganic Chemistry. The occurrence of molecular clusters, like fullerene C60, constitutes a fundamental feature midway between the chemistry of isolated chemical compounds and that of the elements.

In medicine, for example, a cluster can refer to a severe headache that can occur several times in a day, whereas, in astronomy, clusters are usually associated with stars and galaxies. Clusters also are associated with bombs, music, and computers. However, to physicists and chemists, the word cluster has come to mean a group of atoms or molecules formed by interactions ranging from very weak van der Waals contacts to strong ionic bonds.

Clusters of volatile constituents are frequently formed by supersonic expansion through nozzles or, in the case of ion clusters, by sequential growth in low-pressure gases available in ion sources or flow-tube reactors. The intensity of the mass spectra carries information on the relative stability of the clusters. The relative stability also can be studied by reacting the clusters with various reagent gases and re-examining the intensity of their mass peaks. It is always dangerous to attempt to predict the course of development of an active and ever-growing field, but it is certainly safe to state that cluster science has a long and fruitful life expectancy, bridging ideas of interest between nearly every scientific discipline.

Clusters and polynuclear compounds have perhaps been regarded for a long time as fascinating chemical oddities. The exponential growth of their chemistry has been made possible by the advent of X-ray crystallography and many other spectroscopic techniques. The term “metal atom cluster” was introduced in 1964 by F. A. Cotton to designate a finite group of metal atoms held together mainly or at least to a significant extent, by metal-metal bonds. That was necessary in order to differentiate this emerging class of compounds from polynuclear complexes in which the metal centres are held together exclusively or mainly by bridging ligands.

Owing to the above situation, even the thousands of clusters and polynuclear compounds, which have been so far individuated and characterized, represent only the tip of the iceberg. In the following sections, a few representative classes of these molecular species will be described with the exclusive underlying intention to give some flavour of their chemistry. The material is organized so to distinguish between clusters and polynuclear compounds, according to the extended definition given at the beginning of the introduction.

Cluster compounds contain metal-metal single or multiple bonds and form rings or linear chains. Apart from containing σ and π bonds, cluster complexes also display δ bonds. Cluster compounds are formed by almost all the metal atoms, metal clusters consisting of transition metals are known in large numbers. These metal-metal bonds containing complexes can be homo-nuclear, i.e. consisting of one type of metal atoms, and hetero-nuclear which consist of two or more types of metal atoms. Cluster complexes can be synthesized by various methods such as pyrolysis of carbonyl clusters, nucleophilic attack on clusters, reductive elimination and attack of metal precursors on multiple bond containing clusters. Cluster compounds display a variety of reactions. The products of these reactions are sometimes unexpected. The types of reactions that cluster complexes undergo are reactions with electrophiles and nucleophiles, oxidative addition reactions and reactions on the metal-metal multiple bonds.