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Inorganic Chemistry: A Prestigious History and a Bright Future

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After Werner proposed the theory of coordination compounds in 1893 and received the Nobel Prize in Chemistry in 1913 for his work on the linkage of atoms in molecules, there was an enormous growth of research interest in coordination chemistry, a major branch of inorganic chemistry, leading to a plethora of coordination compounds that has been mainly dominated by transition-metal complexes. These complexes were popular given the unlimited combination of ligands of different denticities and bonding modes, a variety of oxidation states, and the diversity of colors, properties, and reactivities. There was an era when researchers focused their efforts in synthesizing and studying huge libraries of transition-metal complexes. The field has increasingly matured with the seminal developments in theories of chemical and metal–ligand bonding, which have evolved through the valence-bond (VB), crystal-field (CF), molecular-orbital (MO), and ligand-field (LF) theories that form the basis for the understanding of structure and bonding in coordination chemistry. The seminal work by Pauling, which led to the Nobel Prize in Chemistry being awarded to him in 1954 for his research into the nature of the chemical bond, laid the foundations in this field. This was further enhanced by work associated with at least three other Nobel Prizes in Chemistry related to bonding, electronic structures, and theories, namely to Mulliken, Fukui and Hoffmann, and Lipscomb. Equally important is the development of electron-transfer reactivities of transition-metal complexes with diverse oxidation states. This has benefited from the elegant works of Taube and Marcus. An exciting development emerged when ferrocene, first made by Pauson and Kealy in 1951, was determined to have a sandwich structure, leading to the Nobel Prize in Chemistry to Fischer and Wilkinson. This has accelerated the parallel growth of research interest in organometallic chemistry, another important branch of inorganic chemistry involving the metal–carbon bond.

Coordination and organometallic chemistry has expanded its scope and horizon to focus not only on the importance of novel bonding and structures, but also to their many functional properties and aspects. These span areas that are at the interfaces of inorganic chemistry, other branches of chemistry, supramolecular science, biology, medicine, catalysis, materials, energy, and the environment, all of which form an indispensable part of our daily lives. For example, the pioneering development of the LF theory and the understanding of electronic transitions and spectroscopy have helped our understanding of colors in transition-metal complexes and their excited-state photophysics and photochemistry. Early works were focused on LF excited states and their reactivities. With the discovery of photoredox reactivities characteristic of the triplet metal-to-ligand charge transfer (MLCT) excited states, there has been a huge interest in the discovery of new MLCT chromophores of Ru^{II}, Os^{II}, Re^{I}, Ir^{III}, Cu^{I}, and Pt^{II} polypyridines. Photoredox reactivity studies are no longer just confined to the understanding of dynamics and mechanisms, but they are now becoming increasingly employed for photosensitization and as visible-light photoredox catalysts for organic synthesis and even natural product synthesis. The rapid development of spectrophotometers and lasers, together with the search for long-lived triplet excited states for efficient organic light-emitting diodes (OLEDs) and optical displays, systems for efficient charge separation for artificial photosynthesis, photochemical H_2O splitting, and CO_2 reduction, photocatalysis, dye-sensitized solar cells (DSSCs), photodynamic therapy, photocaging and uncaging of small molecules for drug delivery, and luminescence sensing and biolabeling, have expanded the scope of inorganic photophysics and photochemistry to areas beyond chemistry. These are just a few of the many examples of how inorganic chemistry has evolved from fundamental studies to the forefronts of interdisciplinary research.

Similarly, other areas of coordination and organometallic chemistry have evolved significantly. For example, various other electronic and optoelectronic applications have been developed, such as organic transistors, spintronics, and memory. Single-molecule magnets, metal–organic frameworks (MOFs) for H_2 and CO_2 storage, supramolecular metallacages and metallamacrocycles for host–guest interaction and supramolecular catalysis and even for sorption of unconventional molecules for structure determination, micro- and mesoporous materials and clusters for catalysis, and metal catalysts for small-molecule activation or N_2 and CO_2 fixation are other examples. A number of these materials have benefited from their unique elec-

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tronic configuration, redox properties, coordination chemistry, and geometries. Organometallic complexes have played important roles in metal-catalyzed organic reactions, which are no longer only dominated by precious-metal catalysts, and the exploration of earth-abundant metals (such as Fe, Co, and Mn) as catalysts has attracted huge interest. Metal complexes that were not considered in the past as "reactive" such as those of Au are now well-established as catalysts for organic transformations. There has been an increasing interest in ligand design beyond the conventional systematic modification of its electronic and steric influence. What was considered to be impossible or elusive has now become feasible. "Unusual" coordination numbers or geometries of d^n electronic configurations are no longer uncommon as the design of ligands can force certain distorted geometries, leading to unconventional reactivities and properties. The former perception of the rather passive or innocent role (other than exerting electronic and steric influence) that ligands play has also been overturned through the use of noninnocent or reactive ligands, leading to activation of the ligands or their participation in bond activation and catalysis. These have opened up fascinating new opportunities of unexplored structures, bonding, and chemistry. Their relevance to polymer synthesis, such as in Ziegler–Natta polymerization and ring-opening metathesis polymerization, has also expanded their scope to materials science.

Main-group and solid-state chemistry are of growing importance and potential. Exciting advancements have been made in terms of new chemistry and structure and bonding associated with main-group elements. Compounds containing Group 13–16 elements play important roles as electronic, optical, and energy-storage materials, and catalysts. Two-dimensional graphenelike materials, such as MoS_2, have aroused much interest in energy applications. Perovskites have attracted revived interest for the development of DSSCs and mesosuperstructured solar cells. Similarly, metal oxides and chalcogenides are playing important roles in nanoscience as quantum dots, nanostructures, photo- and electrocatalysis, fuel cells, and as electrodes and battery materials. Frustrated Lewis pairs (FLPs) involving main-group elements have also offered new opportunities in organic synthesis and catalysis.

Inorganic chemistry also plays a key role in biology- and biomedical-related research. One of the best-known examples is *cis*-platin, a simple coordination complex, whose discovery has aroused enormous interest in the discovery of metallodrugs for anticancer therapy. This research has come a long way from the basic understanding of coordination chemistry, geometrical isomerism, substitution reactions to its binding to DNA, drug action and mechanism, and chemical biology. Apart from development of newer generations of *cis*-platin-type drugs, this field has further been extended to Pt^{IV} prodrugs and targeted delivery, as well as metallodrugs of other metals such as Au, Ru, and Os for tackling Pt-resistant cancers. Multimodal imaging has also attracted much interest and coordination complexes of d- and f-block and main-group elements have been developed. Lanthanide-doped upconversion nanoparticles that can be excited in the NIR region have also gained much attention in luminescence bioimaging and therapy. The understanding of the involvement and role of metals in biology, for example, Li and Zn in neuroscience, Cu in diseases associated with amyloid protein aggregation such as Alzheimer's disease, and many of the important roles that trace metals play in biology and for the maintenance of life, are topical issues. The importance of inorganic chemistry in biology and health science can no longer be ignored and will certainly attract further attention for this branch of chemistry from the pharmaceutical industry.

Apart from the state-of-the-art advancements in spectroscopy and characterization techniques, the rapid growth of computational chemistry has also accelerated the development of inorganic chemistry, thanks to the development of the density functional theory (DFT) and computational methods, which led to the Nobel Prize in Chemistry being awarded to Kohn and Pople. Not only does computational chemistry help in advancing the knowledge in structure and bonding, electronic structures, spectroscopy and mechanisms, but also in the understanding and prediction of material properties and biological activities.

What has been described is by no means exhaustive or comprehensive, not even at the molecular level. Furthermore, supramolecular chemistry and assembly of molecules through non-covalent interactions will further expand the diversity to hierarchical structures and assemblies beyond the molecular level.

I hope the community has come to realize the significance and impact that inorganic chemistry has made not only in the current developments in the field of chemistry alone, but also in the fields of materials science, energy and sustainable chemistry, biomedicine and catalysis.

While we still keep our identity as inorganic chemists, the sharp demarcation between the divisions of different subject disciplines or subdisciplines is no longer relevant. While some people might have mistakenly thought that inorganic chemistry has become a less popular discipline or has now a smaller community, it has actually redressed itself as a chameleon, taking on its existence in many other forms, expanding its horizons beyond traditional and classical inorganic chemistry into nanoscience, materials, energy, environmental science, chemical biology, catalysis, and beyond.

I believe that with the creativity and wisdom of the chemists as well as the versatile state-of-the-art methods and techniques, this is just the beginning of the many adventures and exciting journeys that an inorganic chemist can take. There will be many more scientific developments and a wealth of knowledge and opportunities lying before us that are beyond our imagination.

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