

Directions in inorganic chemistry *

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Abstract

This article is a personal account of the origin and nature of inorganic chemistry. The inherently interdisciplinary nature of modern inorganic chemistry is stressed.

Key word: Inorganic chemistry.

Preamble

I consider myself fortunate to be able to speak to this congregation of scientists and technologists coming from diverse disciplines. At the same time, I realise that the details of any particular subject area can only tax the patience of such an audience. I shall, therefore, use a coarse brush and outline only the main features and movements of my subject area, inorganic chemistry. This is a personal account and is, therefore, limited and tinted by my own perceptions. Please do bear with me on this.

A late starter

In essence, chemistry is a molecular science. The purpose is to understand the properties and transformations of substances in terms of molecular structure and bonding. Rudimentary concepts of molecular structure started to appear only a hundred or so years ago. For this reason, chemistry emerged as a science much later than subjects like astronomy and physics which could flourish on macroscopic rationalisations. The following statement of Immanuel Kant made in 1786 is symbolic of the times two hundred years ago: "Chemistry is nothing more than a systematic art . . . never a true science, because the principles thereof are solely empirical . . .". It was a time when people like Galileo and Newton were long gone leaving behind a legacy of

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astronomy and physics. It was also a time when chemistry, a time-old captive of medicine and magic, had just started to limp leaning on the shoulders of people like Priestley and Lavoisier towards its rebirth as a science. We list below a small group of findings that deeply influenced the development of chemical science in the first half of this century.

Pre-1930

The periodic table

Concept of valence polyhedra

Role of electrons in the chemical bond.

1930s and 1940s

Quantum theories of bonding

Use of physical methods

Concepts of reaction mechanisms.

The activity triangle

In Fig. 1, chemistry is stylised as a moving arrowhead, triangular in shape. The three corners represent three main types of activities and the sides symbolise two-way communication between pairs of activities. The motion of the arrow is fed and propelled by items like those stated below the triangle. Sophisticated measuring techniques and equipment, particularly those revealing structures, have strongly contributed to progress. Good examples are the spectroscopic and diffraction techniques. A very important support for movement is the growing interface between chemistry and other disciplines, particularly physics and biology. The primary motive

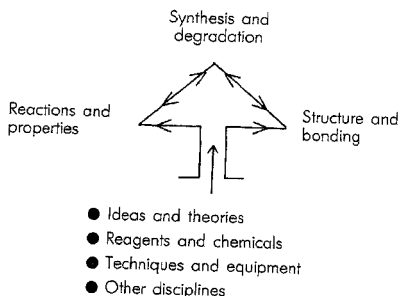


FIG. 1. The activity triangle.

element is, of course, a good chemical idea without which the activity triangle can reach nowhere.

Unity in diversity

Division of a subject area into islands of specialisations is a necessary evil of modern science. Two major islands in chemistry are organic and inorganic. In the former, the activity triangle is centred on carbon and in the latter on other elements. Understandably, organic chemistry became a systematic science much earlier than the far more heterogeneous inorganic chemistry which has to deal with so many elements. Here, unification needed mature ideas of chemical bonding and structure based on quantum theory. This occurred to a considerable extent during the forties. The fifties have been called the renaissance period of inorganic chemistry.

Truly speaking, an element of heterogeneity still persists and it is best taken as a positive feature grained in the very nature of inorganic chemistry. This has added an interdisciplinary bias to the subject. Inorganic chemists have to tread freely in the domains of theorists, spectroscopists, crystallographers, biologists, physicists, material scientists and others. Inorganic chemistry is an epitome of unity in diversity.

The Nobel view

The movement of a subject area with time can be assessed in different ways. A quick but often useful way is to take a view of the Nobel Prizes. Since our time here is short we shall follow this approach. In Table I we have listed a few selected Chemistry Prizes grouped in a particular manner which reflect the growth pattern of inorganic chemistry. Many of the listed laureates cannot be called inorganic chemists in the traditional sense but their work has supplied directive to inorganic chemistry. There is no paradox here: inorganic chemistry draws from wherever it can. This point has already been stressed earlier. We now examine the area items of Table I.

Discovery of elements

In 1904, William Ramsay received the Prize for the discovery of the noble gases in air and more Prizes followed on the discovery of elements and isotopes. In 1951, the Prize was given for transuranium elements. Discovery of elements made no further new history and this topic has become a part of the heritage of inorganic chemistry. The importance of radio elements and the emergence of atomic energy programmes led to coinage of combinations like 'inorganic chemistry and radiochemistry' or 'inorganic and nuclear chemistry'. The components, however, did not integrate well over the years and such combinations are no longer popular.

Directed valence and bonding

Alfred Werner was trained as an organic chemist but was destined to pioneer something else. He suggested that valences of metal ions are directed in space in a

Table I
Selected Nobel Prizes in chemistry

<i>Discovery of elements and isotopes</i>		
1. William Ramsay	1904	Noble gases
2. Henri Moissan	1906	Fluorine
3. Marie Curie	1911	Radium and polonium
4. Harold C. Urey	1934	Heavy hydrogen
5. Jean Frédéric Joliot and Irène Joliot Curie	1935	New radioactive elements
6. Edwin M. McMillan and Glenn T. Seaborg	1951	Transuranium elements
<i>Valence and bonding</i>		
7. Alfred Werner	1913	Linkage of atoms
8. Linus C. Pauling	1954	Nature of the chemical bond
9. Robert S. Mulliken	1966	Molecular orbital method
10. William N. Lipscomb Jr	1976	Structure of boranes
11. Roald Hoffman and Kenichi Fukui	1981	Course of chemical reactions
<i>Organometallic chemistry</i>		
12. Victor Grignard	1912	Grignard reagent
13. Karl Ziegler and Giulio Natta	1963	High polymers
14. Ernst O. Fischer and Geoffrey Wilkinson	1973	Sandwich compounds
15. Herbert C. Brown and Georg Wittig	1979	Boron and phosphorus compounds for organic synthesis
<i>Catalysis and electron transfer</i>		
16. Paul Sabatier	1912	Metal particles as hydrogenation catalyst
17. Fritz Haber	1918	Synthesis of ammonia
18. Irving Langmuir	1932	Surface chemistry
19. Jaroslav Heyrovský	1959	Polarography
20. Henry Taube	1983	Electron transfer reactions
<i>Bioinorganic chemistry</i>		
21. Melvin Calvin	1961	Carbon dioxide in photosynthesis
22. Max F. Perutz and John C. Kendrew	1962	Protein structure
23. Dorothy C. Hodgkin	1964	Biochemical structures
24. Donald J. Cram, Jean-Marie Lehn and Charles Pedersen	1987	Molecules with structure-specific interactions
25. Johann Drenthofer, Robert Huber and Michel Hartmut	1988	Structure of photosynthetic reaction centre

definite manner such as octahedrally for trivalent cobalt. The metal and the six groups (ligands) attached to it by these valences constitute a 'coordination complex'. Very little was known about the origin of chemical bonding and the basis of molecular shapes at that time. Werner's idea of valence polyhedra crystallised from analysis of relatively simple chemical facts. It was a creative flash of rare beauty, probably triggered by the tetrahedral carbon of organic chemistry. It brought order into a large volume of available information and it led to major predictions. Werner was an experimentalist and a synthetic chemist of rare ability and went on translating his

predictions into practice. For example, he predicted and experimentally proved that optical activity is not a special feature of carbon compounds but is a general property of unsymmetrical polyhedral binding.

After the advent of quantum mechanics, directed valence and valence polyhedra appeared as natural consequences of the shape, number and energy of wave functions. Combined application of theoretical studies and experimental methods has since led to deep understanding of molecular structure and chemical reactivity. Several Prizes have been won on the way. This approach forms a vital component of research in inorganic chemistry. It provides key generalisations and suggests new possibilities.

Organometallic chemistry

Victor Grignard was a contemporary of Alfred Werner. He discovered a remarkable class of reactive compounds containing the magnesium-carbon bond. These turned out to be versatile reagents for synthesis of numerous organic compounds. Even more importantly these demonstrated the feasibility of facile formation of the metal-carbon or organometallic bond. Organometallic chemistry has since made big strides disclosing many fascinating structures and reactions and claiming several more Prizes. Ziegler and Natta used titanium organometallics to achieve the polymerisation of ethylene into polyethylene. Fischer and Wilkinson made molecules that looked like sandwiches. Brown and Wittig used organoboron and organophosphorous compounds for synthesis of organic compounds. And the story goes on.

Because of its phenomenal growth, organometallic chemistry is often considered as a distinct branch of chemistry. But that is only a matter of convenience. This chemistry is a true confluence of organic and inorganic chemistry. Inorganic chemists necessarily have much to learn and much to contribute here.

Catalytic and electron transfer reactions

Finding a good catalyst for a good chemical reaction and understanding its mode of action can be a chemist's dream. Paul Sabatier who shared the 1912 Prize with Victor Grignard established the utility of metal surfaces as catalysts for hydrogenation of organic compounds. Fritz Haber developed the catalytic synthesis of ammonia from nitrogen and hydrogen. Irving Langmuir provided rationale for the chemistry of surfaces. Today, the science of surfaces and catalysis plays a major role in inorganic chemistry.

Quite commonly the catalysts are inorganic substances but the reactants and products are organic. Like organometallic chemistry, catalysis also combines organic and inorganic chemistry intimately. In recent years, new spectroscopic techniques have made it possible to examine directly the nature of bonding and activation of molecules on surfaces including those of catalysts. Some catalysts which are molecular in nature can function homogeneously in the same phase that contains the reactant(s). In such cases, one is dealing with molecules only (no surfaces). This can

make the understanding of catalytic function easier and in turn can help in looking at the nature of heterogeneous surface reactions. For example, homogeneous catalysis by a metal cluster molecule (several metal atoms bonded by ligands) can possibly be used to simulate a reaction on the surface of the same metal. In addition to its catalytic significance, cluster chemistry is structurally most fascinating.

A reaction type that is ubiquitous in inorganic chemistry and that keeps researchers busy is electron transfer from one molecule or ion to another. Many reactions of life involve electron transfer and these are often catalysed *via* changes in enzymatic metal valence. Henry Taube received the Prize for his work on the mechanism of electron-transfer reactions. Jaroslav Heyrovský won the Prize for discovering polarography, an electrochemical method for studying electron transfer at electrodes. This method and its later variants have added new dimensions to the study of electron-transfer reactions.

Bioinorganic chemistry

At this time, this area is witnessing frantic activity. The purpose is to unfold the role of metallic and nonmetallic inorganic species in the chemistry of life. The topics to be covered in a major international conference on bioinorganic chemistry due in 1991 can provide some of the flavour: metal recognition, storage and transport; electron transfer; metals, gene expression and regulation; biomineralisation; complexes with DNA; metals and medicine; trace elements and nutrition; toxicological and environmental aspects.

Biological systems are generally very complex. Structure determination is often difficult and requires considerable ingenuity. It is, therefore, not surprising that the bioinorganic-related Prizes have often gone to outstanding crystallographers. With the intense activity that is going on, it is hoped that some Prizes will start going to chemical aspects of bioinorganic chemistry. A beginning has already been made with the 1987 Prize given for the design of model molecules capable of structure-specific interactions. Such interactions form the basis of molecular recognition which is the crux of the specificity of biochemical reactions.

In general, studies of models and analogues—molecular species that are not quite like the complex biological system but that have similar structural and/or functional features—form the first stepping stone in bioinorganic chemistry. Being chemically simpler a good model can go a long way in giving a good glimpse of what happens in the real system. For example, metal-sulfur models are revealing a lot about sulfur-coordinated metallo-proteins. Model manganese compounds are going a long way in telling the nature of the photosynthetic water-splitting reaction. This list can be made very long. A precious byproduct of model compound chemistry is the enrichment of synthetic inorganic chemistry.

Table II
Current scenario of inorganic chemistry

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1. Synthesis and characterisation of new compounds
 2. Structure, bonding, theory and correlations
 3. Reactions and catalysis
 4. Organometallic chemistry
 5. Bioinorganic chemistry
 6. Chemistry of solids and materials
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Other topics, summary and conclusion

We have just mentioned synthetic inorganic chemistry. This forms the top corner of the activity triangle (Fig. 1). It is evident that chemical synthesis, *i.e.*, making of compounds and materials constitutes the most important primary activity which feeds the other activities.

The area of inorganic solids and materials should be mentioned separately to stress its importance. Many fascinating things are happening here and more and more inorganic chemists are turning towards it. The recent developments in high- T_c oxide superconductors is a good example of what wonders inorganic solids can perform.

We can now summarise the main facets of today's inorganic chemistry (Table II).

We conclude by asking and partially answering an important question. How are we doing in India? Being an optimist, I would stress the positive things first. Publications from India in *top* research journals of inorganic chemistry have significantly increased in recent years. A national symposium on inorganic chemistry is being held every two years -- the fourth one is due in 1991. A workshop on bioinorganic chemistry was held recently. These activities are helping in establishing contact among workers and in increasing awareness. More and more young workers below the age of 40 are becoming visible. Though there are world-class groups in the country, unfortunately, their number is not large. The total Indian impact is, therefore, not as good as it could be.

Acknowledgement

I must express my gratitude to the Jawaharlal Nehru Centre in general, and its President, Professor C. N. R. Rao, in particular, for giving me this opportunity to present something that is very dear to me.