Indian Journal of History of Science, 27(4), 1992

DEVELOPMENT OF INORGANIC CHEMISTRY IN INDIA DURING 1900-1980

R.C. MEHROTRA

Vice-Chancellor, Allahabad University,
Allahabad-211 002

Modern research in inorganic chemistry was initiated in 1896 with the publication *"Uber Mercuronitrit"* by Acharya Prafulla Chandra Ray. Calcutta remained the only active school of inorganic chemistry research in India for the next seven decades. From the twenties to forties of this century, Professor Priyadaranjan Ray and his coworkers made outstanding contributions on many topics, including Biguanide Complexes. In the early thirties, he developed two new analytical reagents, quinaldinic and rubeanic acids; work on these two reagents was taken up in many chemical laboratories throughout the world.

With the renaissance of inorganic chemistry on the world scene, the last three decades have witnessed considerable change in the direction of inorganic chemistry research in India. A number of active research groups are engaged in investigating various aspects in specialised areas of inorganic chemistry even with the meagre resource at their disposal. The favourite problem of research has been generally related to coordination chemistry and the study of metal complexes in solution and in solid state. Unfortunately, however, the gap between Indian and international standards of research in inorganic chemistry has widened further during recent years. This may partly be attributed to the lack of sophisticated instrumental facilities, which have started to improve only in the last few years.

A review of progress in inorganic chemistry in the country is attempted in this paper, dividing the topic into three sections:

(i) Area of considerable activity,

(ii) Area of weak activity, and

(iii) Emerging areas in which there is very little activity so far.

This is followed by an analysis of the contributions of the Indian chemists to the world literature in inorganic chemistry during the last few years.

1. INTRODUCTION

In his usual excellent style, my learned teacher, late Prof. W. Wardlaw, while delivering the Presidential Address at Belfast meeting of the British Association in 1952 remarked, "At intervals during the last half century, prophets have confidently predicted the demise of Inorganic Chemistry....." The data presented by Prof. Noyes, Editor of the *Journal of the American Chemical Society* on the basis of articles submitted and published in that journal placed the investigators who identified themselves with inorganic chemistry in rather an unenviable position. According to

him, although the number of papers submitted had not changed significantly over the years 1952-55, the number of papers published had decreased; the rejection rate for papers classified as inorganic had risen and in fact, exceeded that of all other fields. In the words of Noyes himself: "The main field out of line with others is inorganic chemistry and the editors think that a study should be made of the reason for this. Certainly some very poor inorganic manuscripts are received." The situation has changed spectacularly for the better in the last three decades and many novel and exciting branches of chemistry, e.g., cluster compounds, bio-inorganic and organometallic chemistry are the areas which are progressing at the fastest rate in the whole of chemistry.

2. India's Contribution to Inorganic Chemistry

Leaving the early contributions of Indians in the field of (i) metallurgies of gold, silver, iron, lead and tin (*Yajurveda*), (ii) metallic calces (*Charaka*), (iii) alkalies (*Suśruta*), and (iv) medicine (*Vāgbhaṭa*) particularly employing mercury derivatives (*Varahamihira*, 6th century; and *Chakrapani* 11th century) the development of organic chemistry in modern times commenced in this country with the publication of the research paper "UBER MERCURONITRIT" in *Zeitschrift fur anorganische Chemie* by late Acharya Prafulla Chandra Ray in 1896. A year later, two research communications on "Conversions of hypochlorites into chlorates" and "Decomposition of mercurous chloride and the estimation of free chlorine" by Professor Jyotebhushan Bhaduri appeared from the same laboratory of Presidency College, Calcutta. Calcutta remained the only active school of inorganic chemistry research in India during the next few decades. From the twenties to forties of this century, Prof. P.C. Ray made outstanding contributions on 'Biguanide Complexes'; in the early thirties, he developed two new organic analytical reagents, quinaldinic and rubeanic acids. Work on these two reagents was taken up in many chemical laboratories throughout the world soon after.

The last three decades have experienced considerable change in the direction of inorganic chemistry research in India. A number of active research groups are engaged in investigating various aspects in specialised areas of inorganic chemistry even with the meagre resources at their disposal. The favourite problems of research have been generally related to coordination chemistry and the study of metal complexes in solution and in solid state. Unfortunately, however, the gap between Indian and international standards of research in inorganic chemistry has widened further during recent years. This may partly be attributed to the lack of sophisticated instruments, the facilities for which started to improve only in the last few years.

(i) Coordination Chemistry

Coordination chemistry represents the most active branch of inorganic chemistry and is being studied in almost all universities and IIT's. Of the total number of papers published by Indian authors in Indian and foreign journals, nearly 75% deal with some aspect of coordination chemistry.

Coordination chemistry has indeed developed into an inter-disciplinary subject, as it is concerned with tackling of problems in physical, organic, biological and medicinal chemistry. Research in India can be categorised under the following broad headings:

(a) Metal complexes in solution

(b) Non-aqueous solvents

(c) Synthesis of new ligands

(d) Chemistry of lanthanides and actinides

(ii) Synthetic Inorganic Chemistry

(a) Alkoxides, carboxylates, B-diketonates, etc.

(b) Sulfoxides and complexes with sulphur ligands

(c) Complexes with acceptor ligands like tertiary phosphines, arsines, carbon monoxide and hydrocarbons.

(d) Complexes of Schiff's bases and other similar ligands

(e) Metal ion hydride, dioxygen, dinitrogen, nitrosyl and similar complexes with small molecules.

(f) Inorganic preparations.

(iii) Organometallic Chemistry

There are very few centres of organometallic research involving synthesis of compounds with metal-carbon bonds. Organometallic compounds of the main group elements have been studied at a few centres, notably the Universities of Delhi, Lucknow and Rajasthan. Organo-tin and lead compounds have been studied at Lucknow University, while organic compounds of some other fourth group elements have been investigated at IIT, Kanpur and BHU. NCL has been interested in organoaluminium and organotitanium compounds. Metal carbonyls, particularly of the sixth group elements, have been studied at the University of Gorakhpur and Gurunanak University. Some work on complexes of cyclopentadiene, cyclooctatetrene, etc. has been reported from the University of Delhi.

There is a great need for upsurge of research activity in this field. There is practically no work on metal cluster compounds. Sigma and allyl complexes of transition metals is another important field which is yet to be taken up in this country.

(iv) Structural Inorganic Chemistry

This is an area of research which has developed at a phenomenal pace internationally. Although much work has not been reported from Indian chemists due to paucity of sophisticated instruments, this area of study is receiving increasing attention at a few centres in the country, notably TIFR, Bombay, IIT, Kanpur, IIT, Madras, IACS, Calcutta and Indian Institute of Science, Bangalore. With the establishment of Regional Instrumentation Centres at Lucknow, Bombay, Madras and Calcutta, most of the sophisticated instruments will now be available for use to the universities and one can expect an increase in research interest in this important field. Some of the most important techniques which have emerged are C^{13}, F^{19}, and P^{31} NMR spectroscopy, Laser-Raman spectroscopy and photoelectron spectroscopy. Photoelectron spectroscopy is by far the most versatile technique and can give valuable structural information about the complexes, both simple and surface bonded. Research in photoelectron spectroscopy has been initiated at IISc, Bangalore.

(v) Inorganic Reaction Mechanisms

Extensive work in this direction has been carried out at the University of Calcutta. The principal field of interest has been the study of mechanism of substitution reactions in coordination compounds. Similar work is being done at Madras University, IIT, Kanpur and IISc, Bangalore. Investigations on the kinetics of some simple and particularly redox reactions involving less common oxidation states of cations have led to the development of some analytical procedures. This type of work has been reported from several laboratories, notably the Universities of Agra, Allahabad, Berhampur, Gorakhpur, Jammu, Jodhpur, Ranchi and Roorkee.

Work can be initiated on the oxidative addition and reductive elimination reaction of d^8 metal ions like Ir(I), Rh(I), Ru(0), Fe(0), and D^{10} metal ions like Fe(-2) and Pt(0). Nucleophilic reactivity of these complexes with several reagents can be studied without the involvement of any costly set-up. Research activity in the kinetics of fast reactions is highly desirable. Interest along these lines has just been started in the country and should be developed.

(vi) Inorganic Photochemistry

Though there are a few good centres of photochemistry of organic molecules in the country, photochemistry of inorganic molecules is at its infancy in the country. Various reactions like ligand exchange, ligand substitution and cyclo-additions can be initiated by excitation by energy quanta equivalent to d-d transition or a charge-transfer band. Photochemistry of sensitizers like $Ru(dipy)_3$ has gained much importance in energy transfer processes and can be studied. Laser-induced reactions with tuned lasers is another emerging area in inorganic photochemistry and is being investigated at BARC. Photochemical studies on inorganic systems are being initiated at IACS, Calcutta and Indian Institute of Science, Bangalore.

(vii) Inorganic Biochemistry

Inorganic biochemistry or bioinorganic chemistry is an emerging area with considerable potentiality. This area has already been developed as a unique discipline internationally. The places where work is being carried out in the country are BARC, and the Universities of Baroda, Indore and Osmania, IISc, Bangalore and IIT, Bombay. Bioinorganic chemistry deals with the interaction of metal ions with biological systems, transport and storage of metal ions, trace metal requirements of biological systems, structure and functions of metalloenzymes, etc. The subject has become important enough to be covered in a semester or two-semester teaching programme at the post-graduate level. Work can be initiated with various model systems and model enzymes. One good example of a model system that depicts the transport of alkali metals in biological systems is the study of 'cryptates', the macropolycyclic cation inclusion complexes. Such complexes are being studied at Indore and IISc. Another potential field of bioinorganic chemistry is the simulation of biological systems, especially pharmacological responses with concentration and accumulation of various complex molecules. Such studies can be taken up in collaboration with medical centres and drug research institutes. Metal ion interactions with peptides, proteins and nucleic acids are being studied at University of Hyderabad, IISc, Bangalore, and IIT, Kanpur.

(viii) Homogeneous and Heterogeneous Catalysis

This is an area of inorganic chemistry that has much R & D importance and should be developed. Research in heterogeneous catalysis is pursued in the University of Poona, NCL, IIT, Kharagpur and IIT, Madras. Research in homogeneous catalysis is being actively pursued at Osmania University and NCL. Most of the work in heterogeneous catalysis is focussed on the catalytic activity of transition metal complex oxides and correlation of catalytic properties with the electronic and lattice properties and kinetic parameters. Work on homogeneous catalysis is centred around hydrogenation, epoxidation, carbonylation, bond migration, oxo reaction, hydration of olefins and Zeigler-Natta polymerizations. Some recent reactions in homogeneous catalysis include olefin metathesis, cyclization on metallic centres and σ- and π-allyl transitions. These reactions have much preparatory value in organic chemistry. One of the difficult problems in homogeneous catalysis was the recovery and recyclization of the catalyst, which has recently been solved by using polymer-based catalysts. These polymer bases are either organic resins or inorganic supports like zeolites, silicates and glass. These polymer-based homogeneous catalysts can be readily recycled and have been found to be much more effective than heterogeneous catalysts in hydrogenation and oxidation. Work along these lines is practically non-existent in the country and should be pursued. Collaboration between national laboratories and universities can be very fruitful in this area of research.

(ix) Inorganic Polymers

Although research in this area has proved to be of industrial importance ever since the development of silicone chemistry, it has remained almost untouched in

Table 1. Research Publications in Inorganic Chemistry

Area	Total No. of papers per year	Percentage of papers of Indian authors published in	
		Indian journals	Foreign journals
1. Coordination Chemistry			
(a) Preparation and analysis only	25	95	0
(b) Spectroscopic studies included	1000	5	7
(c) Detailed structural studies	250	0	2
(d) Kinetics, mechanisms, etc.	300	5	7
(e) Theoretical	60	0	1
2. Bioinorganic Chemistry	100	6	7
3. Rare-earths and actinides	200	9	14
4. Non-transition elements	120	8	15
5. 'Miscellaneous'-preparation and properties	70	15	6

Research Activities in Inorganic Chemistry

Areas of considerable activity	Areas of weak activity	Emerging areas in which there is little activity
1. Solution Chemistry (a) Spectrophotometry (b) Potentiometry (c) Polarography (d) Electrical conductance	1. Inorganic Reaction Mechanism Substitution and other reactions of coordination compounds	1. Coordination Chemistry (a) Nitrogen and oxygen donor complexes (b) Less familiar oxidation states (c) Metal cluster compounds and transition metal chemistry (d) Coordination polymers
2. Synthetic Inorganic Chemistry (a) Alkoxides, carboxylates, betadiketonates, etc. (b) Perchlorate and sulphoxide complexes (c) Complexes of Schiff's bases (d) Phosphine complexes (e) Inorganic preparations	2. Solution Chemistry (a) Mixed ligand complexes (b) Polynuclear formulation and effects of polymerization, hydrolysis, and protonation in metal-ligand equilibria (c) Partition techniques in the study of metal complex equilibria (d) Complexes involving biologically active compounds	2. Organometallic Chemistry (a) Synthetic studies (b) Homogeneous and heterogeneous catalysts (c) Organometallic and inorganic compounds in chemotherapy
3. Inorganic Reaction Mechanism (a) Oxidation-reduction	3. Organometallic Chemistry	3. Bio-inorganic Chemistry
4. Non-aqueous solvents	4. Chemistry of lanthanides and actinides	4. Inorganic Chemistry in Environmental and Marine Research
5. Chemistry of Rare-earths	5. Structural Inorganic Chemistry	5. Alloys and Intermetallic Compounds
	6. Solid State Inorganic Chemistry	6. High Purity Materials
		7. Structural Studies

India. Some work has, however, been reported from the University of Rajasthan. Work on polymetaphosphates is being carried out at Gorakhpur University. Work on free radical polymerization with inorganic complexes is being pursued at Madras University and CLRI, Madras. Work can be initiated in the following areas of inorganic polymers (activity being investigated at the international level): phosphonitrillic and thiazyl halides, fire-retardant fabrics, polyvanadates, polytungstates and polymolybdates and Zeigler-Natta catalysts.

(x) Analysis of Research Publications in Inorganic Chemistry

In Table 1, we have given an analysis of research publications with respect to world trends based on a survey of journals of the past three years. We shall not comment on the figures shown in the table and leave the conclusions to the judgement and imagination of our colleagues. The numbers shown in the table have been rounded off and are subject to minor variations caused by the choice of classification of papers, the exact year considered and so on.