

Facets of Coordination Chemistry

Edited by

B. V. Agarwala

*Rani Durgavati University
Jabalpur, India*

K. N. Munshi

*Nagpur University
Nagpur, India*



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Facets of Coordination Chemistry

*On the occasion of his 70th Birthday Anniversary
To their distinguished mentor and source of constant inspiration*



Professor Arun K. Dey

*From his numerous students, doctoral workers, research associates
and collaborators as an humble gesture of their gratitude
and reverence*

FOREWORD

It is a privilege for me to have been asked to write the FOREWORD for this volume—honouring the 70th birthday of Professor Arun K. Dey—one of India's foremost scientist. He is one of the chemists who contributed most to the development of Inorganic Chemistry in India during the past half century—and specifically to its development at Allahabad University. His broad interest in Inorganic Chemistry have resulted in significant contributions by him and his research group to many fields of inorganic chemistry, including the formation of complexes in solution, the stability and characterisation of complexes; as well as those possessing biological importance, the colloidal behavior of dye ligands, solution kinetics, theoretical chemistry of metal complexes, gravimetric, potentiometric and titrimetric analysis, chromogenic reagents, ion-selective electrodes, chromatography, electrophoresis, solvent extraction and ion exchange.

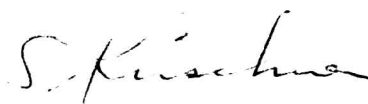
More than 400 publications have been produced by Professor Dey and his research students—and the research from his group has been cited by authors throughout the scientific world. As a result, he received many awards such as the Hill Memorial Prize (1946) of Allahabad University and the Education Minister's Gold Medal (1958) of the National Academy of Sciences of India. In 1982 he was named for the prestigious Acharya P. C. Rây Memorial Lectureship of the Indian Chemical Society and was awarded the medal.

In addition to his important contributions to the scientific literature, mention must be made here of his important contributions to Chemical Education at both the undergraduate and graduate levels—including the training of at least fifty doctoral students, and many master- and bachelor-level degree students. James Bryant Conant, an eminent U.S. chemist and former President of Harvard University, once said that in Education, as in Forestry, few live long enough to see the fruits of their labour. This surely implies that the fruits of the labours of great and important teachers extend very far into the future. If one considers the contributions of not only Arun K. Dey and his research students, but also of his academic children, grandchildren, and great grandchildren—then one can begin to realize the important influence that such a great teacher has, and will continue to have, on the science of Chemistry—and on the future of the world.

Not to be overlooked are Professor Dey's contributions to the administrative side of the science—including his contributions to the International

Conferences on Coordination Chemistry and other chemical conferences, the National Academy of Sciences of India, the Indian Chemical Society, the Indian Science Congress Association, the University Grants Commission, and many other organizations, too numerous to mention here.

Although Professor Dey formally retired in 1983, he has been, and continues to be productive in research and educational activities, and it is hoped that his valued contributions will continue for many years to come.

A handwritten signature in black ink, appearing to read 'S. Kirschner', with a stylized, flowing script.

Stanley Kirschner
Professor of Chemistry
Wayne State University
Detroit, Michigan, USA

PREFACE

Coordination chemistry is now recognised as an independent discipline covering a wide range of areas from the environment to medicine. It no longer involves an academic exercise of synthesising a compound, discussing the bonding and elucidating the geometry, or to identify the various chemical species in solution, or to work out the pathways for complex formation or substitution. The applications of metal complexes in qualitative and quantitative chemical analysis have also been the subject of numerous studies during the past decades.

In the present volume some of the newer significant facets of coordination chemistry by eminent specialists have been highlighted here. The publication is in honour of *Professor Arun K. Dey*, a distinguished teacher and an eminent coordination chemist of India, on the occasion of his 70th birthday anniversary on 20th October, 1992. Fortunately this is also the centenary year of the enunciation of coordination theory by *Alfred Werner* and thus, this year is solemn for coordination chemists all over the world.

The editors had requested a number of eminent coordination chemists to contribute articles on an area of their choice and valuable contributions have been received, which have been incorporated here. Unfortunately, due to the limitation of space, several facets remained untouched.

In the introductory Chapter 1, *Agarwala and Munshi* have presented a concise account of coordination chemistry since its inception. The various developments and facets *viz.* clusters, supramolecular, solution chemistry, crown ethers, coordination polymers and applications in medicine; agriculture etc. have briefly been enumerated.

The fate and levels of hazardous elements in the environment, foodstuffs and in human and marine life have become major problems in environmental research and specially in analytical chemistry. In Chapter 2, *Martin* has critically applied the principles of coordination chemistry to some contemporary environmental problems including the nature of metallic species in the oceans and in fresh water, the red tide problem and carbonate geochemistry.

Basolo in Chapter 3 has described interesting work on metal complexes as synthetic oxygen carriers of biological interest. The initial interest in this area was aroused by *Professor John C. Bailar, Jr.* The cobalt(II) Schiff base complexes were used in defence, welding, cutting and extended an active source to provide oxygen. The low spin Co(II) and Co(III) species are interpreted by

EPR, Raman spectra and X-ray structural studies. A brief discussion on iron capped porphyrin complexes has been made and it has been suggested that CO can bind with them without any marked central steric hindrance. Mn(II) hemoglobin does not bind O₂ reversibly as has been explained on the basis of dissociative ligand substitution mechanism.

In Chapter 4, *Mehrotra* has described a large number of heterometal alkoxides which form a novel series of extraordinary stable polymetallic coordination compounds. The X-ray crystal structure indicating the absence of metal-metal bond and relevant mass spectroscopic and NMR studies are discussed.

Solvent plays a vital role in reactions in solution. *Dash, Nanda and Aditya* in Chapter 5 have highlighted the effects of solvents on the rates and activation parameters of the solvolysis of cobalt(III) complexes. The importance of solvent structure on the activation parameters, ΔH^\pm and ΔS^\pm has been discussed.

Högfeldt (Chapter 6) has introduced a simple model for fitting properties of binary mixtures. The coefficients to each term in the expansion are obtained by least square methods.

In Chapter 7, *Linert* has described bond length variation rules, also referred to as Gutmann rules. The 'pile up' and 'spill over' effects are discussed in terms of donor-acceptor interactions. Salvatochromism of Fe(phen)₂(CN)₂, mixed ligand copper and nickel complexes and other examples are presented.

Among the modern sophisticated instrumental techniques, NMR plays an important role in structural elucidation of coordination compounds. *Khetrapal* in Chapter 8 has described the application of NMR spectroscopy to molecules oriented in liquid crystalline media to study weak molecular complexes. The information obtained from the changes in the degree of order and the molecular structure produced as a result of complex formation is discussed.

In Chapter 9, *Kapoor* has described the application of cyclic voltammetry for the study of electrode reactions. This technique is useful for the study of solution chemistry involving complex formation. The system involving oxidation of ferrocene to ferricinium ion has been discussed.

Chapter 10 by *Liu and Cheng* on chelating polymers attempts in solving environmental pollution. Metal pollution originates for trace contamination in water and soil systems. Specific chelating polymers promise to be useful in the decontamination of aqueous systems such as waste water treatment, sludge recovery etc. Recovery of uranium from sea water by chelating resins which has been a challenging area to many nuclear chemists, has also been discussed.

In Chapter 11, *Fujita and Yoshikawa* have reviewed the work on column chromatographic resolution involving metal complexes mainly done after 1984.

They have succeeded in complete optical resolution of *tris* Si(IV)-phen complex by a chromatographic method and found it to be interesting how the complex cations interact with anions of the eluting agent.

Kauffman published two excellent reviews about the chromatography of metal coordination compounds and included literature published till 1977. *Vuckovic, Tesic and Celap* in Chapter 12 while updating (till 1990) the review discussed the correlation between the composition and structure of transition metal complexes and their R_F values by paper and TLC. The effects of geometrical isomerism, absolute configurations and chelate ligand substituent are considered.

In Chapter 13, *Thomas* has described designs of several polyethers including crown ethers as sensors for ion-selective electrodes. The interaction between macrocyclic polyethers and cations involve three types of coordination which has been incorporated.

Bhattacharya (Chapter 14) described the role of copper as one of the essential trace elements in the biological systems. The classification of copper proteins is made into various types in terms of their role. The oxygen carrier activity of hemocyanin is discussed and the two Cu(I) centres are bridged as indicated by X-ray and EXAFS studies.

In Chapter 15, *Banerjee, Akhbari Shad and Roy* have critically analysed the formation of urinary stones due to the increasing amount of calcium and oxalate in the human system. They are present in leafy vegetables and cannot be precipitated out due to the presence of strong inhibitors or sequestering agents. Though highly sophisticated ultrasound or tiny laser beam therapy is available for the removal of urinary stones, the authors have advocated to adopt inexpensive procedures based on folk medicine and dietary control in which complex formation plays a significant role.

The editors are thankful to all the authors who have responded to their request and sent articles for the monograph. It is hoped that this publication would stimulate further valuable work to enrich the literature and provide materials and techniques for the benefit of mankind.

B. V. Agarwala and K. N. Munshi
Jabalpur and Nagpur
October 20, 1992

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CHAPTER 1

INTRODUCTION : COORDINATION CHEMISTRY AND ITS MULTIFACETS

Badri Vishal Agarwala

Department of Postgraduate Studies & Research in Chemistry, R.D. University, Jabalpur 482 001, India

and

Kailash Nath Munshi

Department of Chemistry, Nagpur University, Nagpur 440 001, India

Alfred Werner, propounded the famous coordination theory 100 years ago and on July 22, 1992 during the 29th International Conference on Coordination Chemistry held at Lausanne, Switzerland (July 19-24) which one of the authors (BVA) had the opportunity to attend, recalled Werner's contributions and a stock was taken of the work done in this field in various parts of the globe. The other days of the conference attended by nearly a gathering of 1000 from all over the world were devoted to several areas of current interest in presentations by participants and this led to interesting discussions. Besides contributed papers, several plenary lectures by experts were delivered, which have been published in a book form 'Perspectives in Coordination Chemistry', Ed. *Williams, Floriani and Merbach* (Verlag Helvetica Chimica Acta, Basel, 1992).

The closing years of the nineteenth century and the beginning of the present century saw a number of remarkable discoveries in the domain of Physics, which had their necessary impact on chemical ideas. When the coordination theory was enunciated, the electron had not been discovered. Electron later became the basis of all theories of chemical bonding. The elucidation of geometry and bonding which were based mainly on preparative procedures received a theoretical foundation from the electronic theory of valency. This was followed by the concept of valence bond theory and electron pair repulsion given by *Sidgwick-Powell*, which are still used extensively, though the ideas have undergone a significant change. The controversy over the extent to which *d*- orbitals participate in σ -bonding has been widely discussed but the *Gillespie-Nyholm* concept of *d*- orbital participation in hybridization is still useful for interpreting the geometry of simple inorganic compounds. The molecular orbital theory for explaining the bonding involved appears to have a better future with the availability of modern computational operations.

Synthesis of coordination compounds provide a challenge to inorganic chemists. This formed the basis of *Werner's* original work and that of his predecessors including *S.M. Jørgensen*. In fact the renaissance of inorganic chemistry in the post second world

war period is closely associated with the renewed interest in coordination chemistry. A survey of literature in inorganic chemistry reveals that at least 70% of the published articles deal with coordination compounds. They provide stimulating problems to be resolved particularly in the context of their stereochemistries.

The burgeoning area of bioinorganic chemistry is centered around the presence of coordination compounds in living systems such as haemoglobins, cytochromes, vitamin B₁₂ etc. Certain metal complexes including those formed by porphyrin act as oxygen carriers and are utilised in the biological transport and storage of molecular oxygen.

Coordination compounds are known to play a vital role in the field of medicine since the discovery of *cis*-platin and carboplatin as anticancer agents. A variety of related platinum(II) and platinum(IV) complexes containing primary and secondary amines were also found to be clinically active. The N-H bonds in these complexes appear to play a crucial role in their mechanism of action. Other complexes of Pt(II) with biologically active N- donor heterocyclic ligands have shown cytotoxicity, single crystal X-ray diffraction studies of complexes formed with styrylbenzazole derivatives have established the structure of a type similar to *cis*-Pt(NH₃)₂Cl₂. However, the toxic side effects such as dose-limiting nephrotoxicity and *cis*-platin used anemia have restricted the use of such platinum complexes as anticancer drugs; only the *cis*-isomer is active and not the *trans*-isomer. The precise action of the drug is not known but it is probable that platinum binds to DNA with guanosine as a base replacing the chloride ions. There are large number of transition and non-transition metal ions associated with DNA while the four elements, Na, K, Mg and Ca are always involved; the concentrations of the first two elements ensure electrolyte balance in the cell and serve as major counter ions of DNA. Another class of compounds are Schiff bases which have been the subject of significant interest in the last three decades in view of their pharmacological importance. They possess remarkable antitumour, antiviral and antimalarial activities which are reported to be enhanced on chelation. The discovery of such compounds and other chelating agents capable of eliminating excessive intake of metal ions from the human body have made important contributions in chelate therapy.

The physicist designs the sophisticated instruments but it is the chemist who derives advantage by making use of them as analytical tools especially for structural elucidations. X-ray crystallography, multinuclear NMR, ESR and Raman Spectroscopy and SQUID are some of the dominant structural techniques used by coordination chemists. The cluster chemistry could not have been developed without such instrumental techniques. Significantly these techniques are now being widely used by medical practitioners as new diagnostic tools. NMR being a non-destructive method is replacing X-ray and is commonly referred to as 'NMR imaging'. SQUID is a fast expanding technique for studies of superconductivity and has become an indispensable technique to detect abnormalities in the human body when combined to the high resolution nuclear magnetic resonance imaging technique; the recent breakthroughs in superconductivity holds a rich promise. Superconductors have the capacity to detect even very weak fields and also to generate immensely powerful magnetic fields.

SQUID is an acronym for Superconducting Quantum Interference Device and is based on Josephson effect. It is essentially formed by a superconducting ring material that has a weak link in an electrical device similar to a transistor. There are some electronic devices which can register magnetic fields. SQUID susceptometer is extremely sensitive; magnetic susceptibility as small as 10^{-12} emu can be measured. They are useful for studies on metalloproteins. Since the human body has very weak magnetic fields (called biomagnetic fields) being continuously produced in nerves, muscles, tissues and organs, SQUID is able to detect it and is thus becoming useful in medical science. It is also possible to study the magnetic fields associated with the lungs, heart, brain and eyes. The SQUID-aided magnetocardiogram can discriminate between the heart-beat rhythms of the pregnant mother and the foetus detecting abnormalities, if any. A useful role for SQUIDS is visualised in detecting iron deficiency in the liver and also abnormal magnetic pollution.

The important contributions made by *Jannik Bjerrum*, *Sillen* and *Schwarzenbach* in the study of complexes in solution are noteworthy and have provided impetus for work throughout the chemical world. Though the formation curves obtained by their schools might be similar, they explained the thermodynamic stability, nature of complexes and interpreted the data by independent procedures. A wide range of complexes formed with ammonia are described in Bjerrum's pioneering book "Metal Ammine Formation in Aqueous Solution". It is commendable to note that the absorptiometric measurements made by him using manual colorimeters 50 years ago, matched well with the findings obtained after the availability of good recording spectrophotometers invented much later. The utility of their studies can be well appreciated by the publication of several volumes on stability constant data brought out by the Chemical Society, London, Plenum Press and others. The solution chemists often comment that it is a difficult task to identify the various complex species formed in solution, whereas it is easier to isolate a compound in the solid state and determine its structural characteristics. However, most of the sophisticated instrumental techniques developed in recent years are also used in the study of binary and ternary complexes in aqueous and non-aqueous media.

Besides the thermodynamic parameters evaluated by the solution chemists, the kinetic aspects have also received attention. Simultaneously, kinetics of complexation reactions also played a role in the development of coordination chemistry in the mid-fifties of the present century. In general, the application of high pressure kinetic techniques to mechanistic studies in coordination chemistry has assisted the determination of the underlying mechanisms in several cases. Detailed account of reactions of coordination compounds in solution, have been published in recent years. Elucidation of reaction pathways through volume profile analysis has been done. The advances achieved in kinetic studies is due to the development of instrumentation which allow the study of slow and fast reactions including flow systems and relaxation techniques at pressures upto 300 MPa. The stopped-flow T-jump, P-jump, ESR, NMR, pulsed-laser and pulse-radiolysis instrumentation are the techniques which cover a kinetic time range from hours and days to nano- and picoseconds. Multi-nuclear NMR such as ^{203}Tl is useful for the study of the ligand exchange reactions between the different cyanocomplexes of thallium(III) in acidic solutions. The exchange is slow on the chemical shift time scale

and the signals are not much broadened by the exchange but the kinetics can be conveniently studied. Mechanisms of macrocyclic metal complexes, porphyrin complexes and ligand substitution reactions of vitamin B₁₂ derivatives have also been studied.

Though compounds containing metal-metal bonds are known for a long time, the chemistry of metal cluster compounds has grown in the last 30 years at a phenomenal rate. They offer a wide range of polynuclear carbonyls, nitrosyls, lower halides, oxides and related compounds. Interest in this area arises from the fact that important iron storage proteins like ferritin and hemosiderin comprise large iron oxide clusters which are assembled step by step with a specific mechanism and requires full understanding. The progress in this area is very rapid and during the last few years several promising synthetic techniques have been developed. Manganese clusters comprising 14 ions, iron clusters containing 16 ions and vanadium clusters comprising as many as 34 ions are known. They can be considered as molecular systems despite the fact that some of these clusters can be considered as small replicas of bulk oxides. These clusters indeed form the individual molecules of the lattice. The vanadium clusters follow the synthetic strategies in which novelty is provided by the magnetic nature of vanadium(IV) ions. Often the interpretation of magnetic properties in such materials is difficult. Cluster compounds are used in catalytic reactions as in the case of the conversion of carbon monoxide and hydrogen into ethylene glycol by rhodium complexes.

An area of particular interest during the last couple of decades has been the design and syntheses of planar, macrocyclic ligands. It was quite exciting when *C.J. Pedersen* announced 25 years ago the synthesis of several macrocyclic polyethers. The alkali metal could be encapsulated by these 'crown ethers' and thus provided the stimulus for future research and opened the way to the cryptands, the spherands, clefts, crypts, the latiriat crown ethers, aza-, thia- crown ethers and channel assemblies. A large number of their derivatives have been obtained with the aim of providing the best possible fit between a specific guest and synthesised host. The relationship between host-guest complexation lies on mechanisms of complexation-decomplexation and needs to be fully understood. Numerous thermodynamic studies have been done on these systems but kinetic studies are scarce. However, ultrasonic relaxation studies have brought information on the rate-determining step of the complexation. Crown ethers and the couple of macrobicyclic crypts are finding increasing applications in liquid-liquid extraction. The latter is useful in phase-transfer catalysis, in stabilising the uncommon oxidation states and promoting unexpected reactions. Resonance Raman experiments and EXFAS studies are useful in locating the terminal donor atoms.

An area termed supramolecular coordination chemistry has emerged recently and is shaping well and progressing with great vigour. Supramolecular chemistry has been defined by *Lehn* as "the chemistry of molecular assemblies and intermolecular bond", or "Chemistry beyond the molecule", bearing organised entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces". Thus, supramolecular chemistry may be considered to represent a generalised coordination chemistry extending beyond the coordination of transition metal ions by organic and inorganic ligands to the binding of all kinds of substrates. This may

be anionic, cationic and neutral species of either organic, inorganic or biological nature.

The field of anion coordination chemistry is expected to yield a great variety of novel structures and properties of both chemical and biological significance. Though the concept of anion coordination chemistry was formulated nearly 15 years ago and initially could not be accepted but in recent years the researches in this area are building up progressively. Various hydrogen bonding coordination patterns have been identified by crystal structure determination and acyclic anion complexones have also been investigated.

The post second world war period has witnessed almost an explosion in scientific activities, as a result of the need of new materials and processes. This has especially been observed in the realm of inorganic chemistry, and has resulted in the emergence of entirely new disciplines, often by the fusion of subjects remotely related to one another. Thus, the new technological advances in fields like nuclear science and space technology have prompted a search for materials with specific properties. Polymer chemistry, which has revolutionized human civilization was hitherto concerned with organic macromolecules, has now overlapped with Inorganic Chemistry to provide a new type of materials called Inorganic Polymers.

The coordination polymers are generally classified as inorganic polymers, but it should be recognized that a large fraction of the ligands employed are, perforce, organic and that consequently, many of the materials involved are really semiorganic or in some cases almost completely organic in nature. There are several kinds of coordination polymers which have been prepared by the interaction of metal ions and organic ligands. Many of these compounds show a thermal stability higher than that of the organic substance employed as ligands in the metal complexes.

The coordination polymers are easily recognized in two categories, one in which the metallic element is an integral part of the backbone and a second in which the metallic element is coordinated to a polymer repeating donor groups. Most of the known coordination polymers fall in the first group and a majority of them can be considered natural coordination polymers, in so far as they were not deliberately made as polymers, but rather, are substances found to be polymeric in the course of their characterization. The second type of polymers are known as synthetic coordination polymers.

The polymers containing coordinated metal ions have been divided into three categories. Firstly, those which are obtained from metal ions and preformed polymeric ligands having coordination sites. Production of polymers using preformed polymeric ligands has not been extensively studied, but the literature contains some interesting applications of this procedure. Secondly those which result when metal ions and ligands combine. The possibility of using reactions of this type depends primarily on the fact that transition metal ions are polyfunctional in character. They are capable of accepting more than one lone pair of electrons and consequently, the reaction with polyfunctional donor molecules resulting in chain or cross-linked polymeric structures. The degree of cross linking in any polymer of this type is governed by the coordination number of the metal and the number of coordinating centres of the ligand. Combination between a *bis*-