Inorganic Chemistry : Research and Teaching : Retrospect and Prospect[†]

D. Banerjea*

A-4/6, Iswar Chandra Nibas, 68/1, Bagmari Road, Calcutta-700 054, India

Introduction

Historically, inorganic chemistry is the oldest branch of chemistry. Classical inorganic chemistry was primarily concerned with the preparation and studies of the properties of all the elements and their compounds, including the simple compounds of carbon. At the beginning of the 20th century two important inorganic chemical industries were established, viz., the Ostwald process (1902) for the production of HNO_3 based on catalytic oxidation of NH_3, and the Haber process (1905) for the manufacture of NH_3 from N_2 and H_2. The developments of inorganic chemistry during the first half of the 20th century progressed rather slowly, but for several reasons much faster developments took place since the 1950s. In the year 1948, of the total number of papers abstracted in the *Chemical Abstracts*, inorganic chemistry constituted only *ca.* 9.8% and this rose to *ca.* 15.8% in 1958. Significant advances in inorganic chemistry since the 1950s have revolutionised the ideas and concepts and have widened the domain of inorganic chemistry, which now extends from solid state science bordering physics to life science at the other extremity. The growth has indeed been explosive and spectacular which necessitated publication of a new journal *Inorganic Chemistry*, by the American Chemical Society, since 1961 (the impact factor, IF, of this journal as per latest available report is 2.7), splitting up of the *Annual Reports on the Progress of Chemistry*, published by the Chemical Society, U.K. (now the Royal Society of Chemistry) in 1968 into Sections A and B (the Section A covering general, physical and inorganic chemistry) and a further splitting up of the *Annual Reports* in 1978 into Parts A, B and C, the Part A being devoted to inorganic chemistry and its allied fields. During 1979 the coverage of Part A was a total of 260 pages as against only 177 pages devoted to inorganic chemistry in 1977 and only 110 pages in 1968, but this increased to 401 pages of the same size in 1986 and 636 in 1997. Much more significant are the total citations : 1776 (in 1978), 2932 (in 1983), and 5370 (in 1994) of which 720 were on inorganic reaction mechanisms, 215 on bioinorganic chemistry and 209 on fullerene chemistry showing the emphasis on these new areas of research. In 1998,

20 major conferences in inorganic chemistry were held world wide, and the International Conference on Coordination Chemistry (ICCC) which had a modest beginning in 1950 has now grown into an enormous size as any look into the Abstract book of the recently held 34-ICCC at Edinburgh (July, 2000) would indicate.

However, a scrutiny of the currently available sources such as the *Annual Reports on the Progress of Chemistry* (ARPC), over a period of last 25 years, indicates that publications of Indian authors (in journals published both in India and abroad) which appeared in these citations annually were only *ca.* 1% of the total citations (of works considered scientifically significant) and papers published in the *Journal of the Indian Chemical Society* appeared in these citations only rarely, but in this respect even the *Indian Journal of Chemistry* (published by the CSIR, New Delhi) is somewhat better. It is indeed a matter of great concern to us that the IF of JICS has now come down to 0.14 with a value of IJC being 0.38, 2.0 for *J. Chem. Soc., Dalton Trans.*, and 1.2 for *Polyhedron* (2.7 for *Inorg. Chem.* mentioned earlier), etc. It is a pity that many of our research workers seek to publish in foreign journals which obviously creams off much of the good work resulting in a lowering of the standards of our national journals. Good work of our top ranking chemists would not be less excellent if these were published in our journals. The author can cite several examples of Indian work published in good ranking foreign journals that met with much adverse criticism, while there are quite a good number of publications in Indian journals that received admirable comments in various Annual Reports and Reviews, Specialist Periodic Reports, etc., and some of these even find a place in modern advanced level books in the subject.

With the growth witnessed since the 1950s there has been a dramatic change in our outlook and approach to the subject as is evident from several important treatises published in subsequent periods, particularly "Inorganic Chemistry" by K. F. Purcell and J. C. Kotz (W. B. Saunders, Philadelphia, 1977), followed by several others from different groups of authors.

Highlight of developments

At the dawn of the 20th century 82 elements were known, a few of which were discovered in prehistoric times, and the rest have all been discovered or synthesised in the 20th century. During 1940-70, the transuranium elements of $Z = 93$–105 were synthesised, followed by $Z = 106$–109 by 1989, and evidence for $Z = 110$–112 were presented by 1996[1a-d] only three atoms of $Z = 111$ were detected in a nuclear reaction between the heavy nuclei Ni and Bi in 1995, and only one atom of $Z = 112$ was detected in 1996 in a nuclear reaction between Pb and Zn nuclei. In 1999 syntheses of a few atoms of elements of $Z = 114$, 116 and 118 have been reported by Russian[1e] and US[1f] groups.

Of the 30 elements known to be essential/beneficial to life, 15 are metals. The distinctive biological roles of many of these elements became established in the later periods of the 20th century, viz. Zn (1940), Cr (1955), Mo and Mg (1956), Se (1957), Sn (1970), V (1971), Li and W (1973), Ni (1974).

Many of the advances in the second half of the 20th century were due to advent of a number of sophisticated physical techniques and equipment which provided precise information about structures and bond features, molecular electron energy levels, etc., to which the classical chemists had no access and as such all their conclusions were based on data obtained by chemical analysis, a few physical properties like magnetic behaviour, dipole moment, etc., and observed reactions. Many such conclusions had to be abandoned or modified based on data obtained by refined methods and techniques in later periods. Sophisticated MO descriptions based on refined spectroscopic energy level diagrams of even simple species enabled to account for marked differences in the affinities of the isolectronic species CN^-, CO and N_2 for binding to a metal, or to explain why, unlike NO_2, there is little tendency for NO to dimerize although both are odd electron molecules with one unpaired electron in their molecular framework, or why the bond order in CO^+ is 3.5 and that in N_2^+ is 2.5 although these are isoelectronic and the bond order is 3 for both CO and N_2, or why BX_3 (X = halogen) exists but not BH_3. It is also possible to account for the bonding in electron deficient B_2H_6, and in species like XeF_2, XeF_4 and XeF_6 discovered in the 1960s the existence of which could not even be conceived by the classical chemists at least till the 1930s.

It is worth noting in this connection that while the Zeise's salt, $K[PtCl_3(C_2H_4)]$ was known since 1827, the nature of the anionic species and its structure were elucidated more than a century later by X-ray crystallographic method (Ouston *et al.*, 1969), confirmed further by neutron diffraction technique (Love *et al.*, 1975). The nature of the Pt-

olefin bond was elucidated by Chatt and Duncanson in 1953 based on an idea originally put forth by Dewar in 1951. This, now well-known, Dewar-Chatt-Duncanson model explains bonding not only in metal-olefin and metal-acetylene complexes but also in a number of other cases as in some complexes of O_2, H_2 and a rare few of N_2 in which these diatomic species exhibit ethylene-like bonding to the metal.

Since the first accurate (*ab initio*) molecular orbital calculations were done on simple diatomic molecules such as LiH in the 1960s the range of molecules that can be described by accurate MO method has expanded rapidly with the advent of modern computers. Computational methods are now making an increased impact on diverse areas of chemistry including inorganic chemistry (*cf. Chem. Brit.*, November, 1990).

Electronegativity concept first introduced by Pauling (1932) has since then been defined in many ways and its precise interpretation is still a subject of ongoing debate[2]. Despite this, Pauling's electronegativity concept (electronegativity values in Pauling scale are widely used) proved very useful to account for a number of observed facts concerning stabilities and reactivities of a variety of inorganic compounds. The VSEPR theory that followed from the suggestions of Sidgwick and Powell in the years upto 1940 and later extended and put into a modern form by Nyholm and Gillespie (1957) has proved to be of much success to account for shapes of different molecular species of similar composition, viz. ICl_4^-, BF_4^-, SF_4 or SF_6, XeF_6, etc. Empirical observations on metal-ligand interactions led Ahrland *et al.*[3a] to classify metal ions (Lewis acids) into classes a and b which was later generalised by Pearson[3b] in the HSAB concept to account for the interactions between different types of Lewis acids with Lewis bases[4]. Chatt[5] offered a rational interpretation for the *hard* and *soft* behaviours based on his concept of ligand to metal pi-bonding (a concept originally introduced by Pauling to account for M=C double bond in the metal carbonyls for which various evidences are available). Schwarzenbach and Shellenborg[6] proposed $MeHg^+$, an ideal soft acid, to set up hardness scale for Lewis bases, while Williams and Hale[7] arrived at the hardness scale for M^{m+} (Lewis acids) using F^- (hard base) and I^- (soft base).

Gutmann[8] introduced a thermodynamic parameter (Donor Number, DN) to express basicities of solvents that account for their relative solvating power. Gutmann[9] extended the concept to include an Acceptor Number (AN) that measures the electrophilic behaviour of a solvent. Drago[10a] criticised the donor number concept as according to him this presents only half of the information available from the Drago-Wayland equation[10b].

Revival of the classical crystal field theory (Bethe, 1929)

and its further sophistication into the ligand field theory by Orgel, Jorgensen, Ballhausen and others during the 1950s to early 1960s is another significant advancement which could provide quantitative interpretations of the features of spectra and several other properties of transition metal compounds that was hardly possible on the basis of the valence bond concept of Pauling (1931) despite initial success of Pauling's views to expain in general the stereochemistry and gross magnetic behaviour of transition metal compounds.

During 1939-47, the four missing elements of the Periodic Table, viz., Tc, Pm, At and Fr (Z = 43, 61, 85 and 87) were produced by nuclear reactions. In 1940, McMillan and Abelson similarly produced the transuranium elements Np and Pu (Z = 93 and 94) which was followed by the production of Am and Cm (Z = 95 and 96) in 1944, of Bk (Z = 97) in 1949 and Cf (Z = 98) in 1950 by Seaborg and coworkers[1]. Scientists of the erstwhile Soviet Union also contributed in the synthesis of several of the transuranium elements, and uptil now the elements upto Z = 118 have been reported (*loc. cit.*). The controversies in naming these elements were set to rest by the International Union of Pure and Applied Chemistry (IUPAC) by a system of nomenclature recommended in 1979[11].

The steady improvement in synthetic methodology allows us to foresee coordination chemistry entering a phase of creative rather than investigative chemistry. The development of complexes for applications in medicine is an obvious example, and a remarkable example being *cis*-platin, *cis*-$PtCl_2(NH_3)_2$, introduced by Rosenberg[12]. This discovery led to a veritable avalanche of research in platinum chemistry and for a continuing search for the most effective anticancer drug[13]. That chelation plays a definite role in the cause and treatment of cancer is a significant development of the 1960s[14]. Synthesis of systems with particular properties has led to significant applications of metal complexes, including organometallics, in technology primarily as catalysts of selective and even specific nature in some cases. In general, coordination chemistry has come a long way from the simple molecular systems that Werner studied, and we do foresee a much wider perspective for coordination chemistry in the years to come. The 1950s saw the beginning of interest in coordination chemistry in biological systems, and now even in the environment[15]. The applications of coordination chemistry continue to grow. The potential of complexation reactions in analytical chemistry, in solubilisation and extraction of metals even from low grade ores, and in the separation of chemically closely similar metals has been widely exploited, and homogeneous catalysis has been a remarkably successful area of application, both in the possibility of activation of otherwise rather inert small molecules

following complexation (as in the cases of H_2, O_2 and even N_2), and, more recently, in the introduction of stereoselectivity by control of the structure of the coordination site and judicious use of weak ligand-ligand interactions. At the recently held 34-ICCC at Edinburgh (*loc. cit.*) S. J. Lippard highlighted the fundamental importance of coordination chemistry in neuroscience (Abstract No. 1171, 34-ICCC). Many drugs are known to be potentiated by complexation with M^{m+} (*cf.* Schubert, "Metal Binding in Medicine", Philadelphia, 1960). Thus, antibacterial activity of 8-hydroxyquinoline is increased significantly by Fe^{III} (Albert *et al.*, 1947), antitubercular activity of isonicotinic acid hydrazide is increased ten-fold by Cu^{II} (Foye and Devall, 1958), carcinostatic activity of many drugs is enhanced by chelation (Kirschner *et al.* 1966); compounds of Au with sulfur drugs have higher antibacterial activity than the parent drugs, many drugs used in rheumatoid arthritis are potentiated by Cu^{II} and become safer in use, and similar effect has been observed for Au^I.

The Inorganic Chemicals Group, a subject group within the Industrial Division of the Chemical Society, U.K., was established in 1972 to promote the industrially relevant aspects of inorganic chemistry. In pursuit of this objective, the committee had organised and run specialist symposia annually in various localities in the U.K., and arranged a more ambitious meeting in London in 1977 at the annual congress to review the inorganic chemical industry as a whole. In this there was an elaborate coverage of the various inorganic chemcial industries in all aspects including their impact on the environment, and the full texts of the lectures and discussions were published[16]. Perhaps, the Indian Chemical Society may think of taking up such a venture. It is, however, worth noting in this connection that no chemical industry in India is ranked within the 50 top chemical industries of the world.

Two sexadentate ligands were first reported in the late 1940s, one provided $N_2S_2O_2$ coordination and is a Schiff base (Dwyer and Lions, 1947, 1950) and the other is EDTA (now widely used), an aminopolycarboxylate, providing N_2O_4 coordination (Schwarzenbach and Ackermann, 1948). EDTA has remarkable ability to strongly complex even Ca^{II} and Mg^{II} which are otherwise rather weak complex formers. Use has been made of the calcium complex of EDTA as a scavenger for removing heavy metals like Pb^{II}, Cd^{II}, etc., in cases of such heavy metal poisoning in humans. Synthesis of an octadentate ligand and its complexes have been described[17]. Calix(n)arenes which are macrocyclic polyphenols having n donor oxygen atoms mimicking some Fe^{III} binding enzymes were reported in 1984[18a,b]. Pyrrole-based analogues of calixarenes have high affinity for halide ions[18c],

the binding is with the N atoms of the several pyrrole rings of the macrocycle through hydrogen bonding interaction, X^------(----HN)$_x$. In 1988. Rebeck, Jr. and coworkers[18d] reported an aminopolycarboxylate type ligand which has exceptional affinity for Ca[II] and Mg[II] ions; a 0.1 M solution of this ligand in CHCl$_3$ extracts >99% Ca[II] and $ca.$ 73% Mg[II] from aqueous phase (brine) having 59 ppm Ca[II] and 24 ppm Mg[II]. Better Fe[III] specific chelators have been synthesized for use as drugs for removal of iron. These have several catecholate or hydroxamate like binding sites[19]. Antitumor activity of Cu[I] complexes have also been reported[20] and Cu[II] antitumor agents have also attracted much attention[21], as also of complexes of Au[I] and Au[III] as antitumor agents[22].

A silver(III) complex of ethylenedibiguanide is the most stable complex of Ag[III] known so far[23a], both thermodynamically[23b] and kinetically[23c]. An interesting reaction that leads to a cationic complex of carbon(IV) was reported by Nyholm and coworkers in 1964[24] :

$$CCl_4 + 2(diars) \longrightarrow [C(diars)_2]Cl_4$$

From the chloride other salts were obtained by usual metathesis and all were found to be typical electrolytes. Pedersen's pioneering discovery (1967) of crown ethers[25] and their affinities towards metal cations demonstrated that effective and selective complexation can be achieved with neutral organic ligands that provide cavities of the appropriate sizes to firmly complex the cations selectively; a metal ion of proper size that fits into the cavity, being neither too small nor too large, is selectively complexed. Many high affinity ligands for complexation of metal cations have since then been reported[26]. The first crown ether to be made was dibenzo-18-crown-6 and several others were made subsequently[27a]. Interestingly, while these have significant affinity for a variety of non-transition metals, they have limited affinity for the d-block metals which are otherwise good complex formers with a variety of ligands[27b]. Several papers have appeared in literature on the likely use of crown-complexed species in analysis, catalysis, synthesis, ion transport separation, etc.[28]. Such macrocyclic ligands help solubilization of inorganic salts like KOH, KMnO$_4$, AgNO$_3$, etc., in organic solvents by their complexing the cation of the salt and are thus useful reagents in organic syntheses. Multidentate macrocyclic ligands that are suitably internally crosslinked with donor atoms correctly positioned in the bridging groups can completely encapsulate metal ions in a cage-like structure. One such class of ligands are the cryptands which form complexes known as cryptates. Several such ligands having O,N donors and O,N,S donors are known[29]. The crown ethers and cryptands have enabled iso-

lation of stable yellow-brown coloured $alkalides$ having M$^-$ (M = alkali metal) and $electrides$ having e^- as the cation charge balancing species in salt-like products, viz. [M(cryp-222)]$^+$M$^-$ (M = Na, K, Rb, Cs) (golden yellow coloured), [Rb(15-crown-5)$_2$]$^+$Na$^-$, [Cs(18-crown-6)$_2$]$^+e^-$, etc., as also stable salts of a variety of Zintl anions, viz. [Na(cryp-222)]$_2^+$E$_5^{2-}$ (E = Sn, Pb) (red-orange), and others having Bi$_4^{2-}$, Sn$_9^{4-}$ Ge$_9^{2-}$, Ge$_9^{4-}$, etc., with [Na(cryp-222)]$^+$ or [K(cryp-222)]$^+$ as the counter ions[30a-d]. But conspicuous also is the isolation of bronze coloured [Li(RNH$_2$)$_x$]$^+$Na$^-$ (R = CH$_3$. C$_2$H$_5$)[30e]. Incidentally, the unusual compound Na$_{23}$K$_9$Tl$_{15}$ was reported in 1996 by Dong and Corbett[31a] which has the Zintl anions Tl$_5^-$, Tl$_7^{3-}$, Tl$_5^{7-}$ and Tl$_4^{8-}$. Isolation of M$^+$Au$^-$ (yellow-brown) from liquid ammonia solution of an alloy of Au and an alkali metal (M = Na, K, Rb, Cs) has also been reported[31b], as also K$_8$M$_{11}$ (M = In, Tl)[31c].

Sepulchrate is another novel encapsulating ligand that can be isolated only as a metal complex, viz., of Co[III], Pt[IV], formed by a condensation reaction of M(en)$_3^{m+}$ with formaldehyde in presence of aqueous ammonia[32a]. The Co[III] complex has a promise as a photosensitizer[32b].

The concept of anion coordination postulated in 1978 met with some initial resistance, but researchers are increasingly active in this area in recent years and anion coordination is building up progressively in its own right[33]. Positively charged or neutral electron deficient groups may serve as interaction sites for anion binding. Starting with the halide inclusion complexes (the $katapinates$, Park and Simons, 1968; and $anion cryptates,$ Graf and Lehn, 1976) poly-ammonium macrocycles and macropolycycles have been studied most extensively as anion receptor molecules. They bind a variety of anions like azide, nitrate, sulphate, phosphate, carboxylates, etc., and selectivities resulting from both electrostatic and structural effects have been noticed. Acyclic anion complexes, patterned after cation complexones with NH$_4^+$ or guanidinium ion groups replacing the carboxylate groups of metal binding complexones have also been investigated[34]. Tetrahedral, octahedral, trigonal prismatic, etc., coordination of the complexed anion has been established by X-ray crystallographic structure determintion in the anion complexes[35]. Halide binding calix(n)pyrroles have been mentioned earlier[18c].

A novel bidentate ligand capable of spanning $trans$-positions in a metal complex has been reported[36a], and considerable advances have been made in template synthesis of macrocyclic ligands of mono-, bi- and polynucleating types capable of complexing one, two or more metal ions[36b]. Also of considerable interest are the metal complexes of O$_2$[37], and N$_2$[38]. Interest in such complexes stems from activation

of these diatomic species due to metal binding. Many such complexes of O_2 are useful for selective oxidation, and as oxygen carrier due to reversible binding of dioxygen. The first authentic dinitrogen complex was prepared by Allen and Senoff[39], $[Ru(NH_3)_5N_2]^{2+}$. Interesting also is the dinuclear complex $[(NH_3)_5Ru\text{-}N\text{-}N\text{-}Ru(NH_3)_5]^{4+}$ having linear Ru-N-N-Ru[40]. Another important compound reported is trans-$[Mo\{Me_8(16)ane\}(N_2)_2]$ having trans-N_2-Mo-N_2 and its structure has been elucidated[41]. However, most interesting are the groups of compounds $M(PR_3)_4(N_2)_2$ and $M(diphosphine)_2(N_2)_2$ (M = Mo, W) reported by Chatt and coworkers[42], some of which release part of the nitrogen as NH_4^+ on treatment with acid (methanol solution of H_2SO_4) at room temperature[43]. This provided an understanding of the mechanism of nitrogen fixation in nature by the Fe-Mo-S enzyme nitrogenase. Incidentally, the structures of both of the components of nitrogenase, viz., the Fe-S protein, the P factor, and the Mo-Fe-S protein the Mo-Fe cofactor, have been elucidated[44]. Available evidence does not indicate formation of any Mo–N_2 bond in the enzymic reaction, and the bonding might be at the Fe site, but that is yet to be established conclusively.

Hydrogen is unique in many respects including the wide variety of interaction with other elements that it exhibits in stable species. Since discovery of the hydrogen bond by Latimer and Rodebush (1920), which involves three-centre-four-electron interaction in the system $^{-\delta}X\text{---}H^{\lambda+}\text{---}Y^{\delta-}$ (X and Y being strongly electronegative), its widespread occurrence in chemistry became gradually recognised and established. But most significant was the evidence for hydrogen bonding in the double helical structure of the DNA that carries the genetic code without which life in any sense that we know of would have been impossible. Without hydrogen bonding, liquid water, so essential to life, would have existed in gaseous form under ordinary conditions (b.p., ca. –73°) and many such drastic changes in properties and behaviour of many species would have been observed. Another novel type of bonding involving hydrogen has been recognised in the 1990s which involves interaction of the type $^{+\alpha}M\text{---}H^{\sigma-}\text{---}^{\beta+}H\text{---}X^{\beta-}$ (X = O, N)[45]. Another novel interaction is known as agostic interaction[46a] first demonstrated by neutron diffraction study[46b] of the compound $[Fe(\eta^3\text{-}C_8H_{13})(P(OMe)_3)_3]^+$ that indicated strong C—H---Fe interaction. Complexes which would otherwise be coordinatively unsaturated (18-electron configuration not attained by the metal) can be stabilized by the interaction of the metal with a nearby C—H bonding pair of electrons in a three-centre-two-electron interaction. Evidence for this is from structural and spectroscopic data that indicates strong M---H—C interaction. By having a share of the electron

pair of the C—H bond in the three-centre-two-electron interaction, the metal attains the stable 18-electron configuration as is the case with $W(CO)_3(PCy_3)_2$ (Cy = cyclohexyl)[46c]. In solution, agostic interactions can be detected by unusual positions for ^1H NMR signals and values of coupling constants J (^{13}C—H). However, many compounds are also known whose structures or spectra give no evidence for such agostic interaction even though there is an empty metal orbital; but evidence for agostic interaction does exist in several cases, and the term now includes all similar cases, M---H—E (E = C, B, Si, N, P, S, Sn, and even Cl and F)[47].

Another type of interaction is the η^2 bonding of H_2 to a metal, first reported in 1984 by Kubas and coworkers[48a] in $W(CO)_3(PPr^i_3)_2(H_2)$. Since then several other known cases have been reported. This class of metal—H bonded compounds are now referred to as nonclassical hydrides in which the M—H_2 bond has a formal analogy to the M—olefin bond (Dewar-Chatt-Duncanson model, loc. cit.), while those with M—H bonds are known as classical hydrides[48b]. The tungsten compound exists in solution in suitable solvents as an equilibrium mixture of $W(\eta^2\text{-}H_2)$ (ca. 85%) and $W(H)_2$ (ca. 15%). Examples are also known in which we find both types of bonding in the same compound, viz., $M(H_2)(H)_2 (PPr_3)_3$ (M = Fe, Ru)[49a]. Some $M(\eta^2\text{-}H_2)$ complexes are strongly acidic[49b], e.g., trans-$Os(\eta^2\text{-}H_2)(dppe)_2$-$(MeCN)^+$ has $pK_a = -2$, it loses proton forming $Os(H)$-$(dppe)_2(MeCN)$. $M(\eta^1\text{-}H_2)$ end-on bonding is also known[49c,d].

While the hydridometal carbonyls were known for many years ($H_2Fe(CO)_4$ reported by Hieber in 1931), the first non-carbonyl compound having metal–hydrogen bond of great stability and that too of a transition metal was reported by Chatt and coworkers[50] in 1957, viz., $Pt(H)(Cl)(PEt_3)_2$, a white solid distillable at 130° (0.01 mm Hg), stable in moist air, and does not react with water or even dil. HCl. It dissolves in aqueous ammonia from which it can be recovered unchanged by evaporation or acidification. But it is a mild reducing agent and precipitates metallic silver from a solution of Ag^+ salt; the Cl in the complex can be replaced by Br, I and SCN. Determination of crystal structure of the bromo compound has established trans-structure[51a]. Preparation of trans-$Pt(H)Cl(PEt_3)_2$ is simple and involves reaction of cis- or trans-$PtCl_2(PEt_3)_2$ with hydrazine hydrate or boiling KOH + EtOH. The analogous arsine complex trans-$Pt(H)Cl(AsPh_3)_2$ has also been reported. Reaction of $PtCl_2(OPMe_3)_2$ with $NaBH_4$ in MeCN gives $Pt(H)Cl$-$(OPMe_3)_2$[51b]. Reacting $(Cp)_2TaCl_3$ with $NaBH_4$, $(Cp)_2$-TaH_3 is obtained and this is stable to acid and is not protonated. But reacting MCl_5 with Na^+Cp^- (excess), one obtains $(Cp)_2MH_2$ (M = Mo, W) and these are readily proto-

nated by acid forming $(Cp)_2MH_3^+$ (the basicity is comparable to that of NH_3). The compounds trans-Fe(H)(X)(diphosphine)$_2$ (X = Cl or H) and trans-Os(H)Cl(Et$_2$PCH$_2$-CH$_2$PEt$_2$)$_2$ have also been reported[52a], as also Re(H)$_7$-(AsPh$_3$)$_2$ and Re(H)$_6$(AsPh$_3$)$_2$(EPh$_3$) (E = Si, Sn)[52b]. Still more interesting are the complexes having only hydride ligand, viz., Na$_2$[PtH$_4$] (red-violet), obtained by heating finely divided Pt with NaH in a current of H$_2$[53a]. While PtH$_4^{2-}$and RhH$_4^{2-}$ are square-planar, K$_3$MnH$_5$ is made up of tetrahedral MnH$_4^{2-}$ and H$^-$ions[53b]. The compounds K$_2$MH$_9$ (M = Re, Tc)[54] are well-known. These are colourless and diamagnetic and are obtained by reduction of KMO$_4$ by K in ethylenediamine. Many metal complexes having hydride bridges have also been reported. Thus, Pt(H)Cl(PEt$_3$)$_2$ on treatment with NaBH$_4$ in MeCN gives [(Et$_3$P)$_2$(H)Pt(μ-H)Pt(H)(PEt$_3$)$_2$]$^+$. Some other representative examples are trans-(Ph$_3$P)(Et$_3$P)Pt(μ-H)$_2$Pt(PEt$_3$)(PPh$_3$)[55], (Me$_3$P)$_3$(H)-Ru(μ-H)Ru(H)(PMe$_3$)$_3$ and (Me$_3$P)$_3$(H)Ru(μ-H)$_3$Ru-(PMe$_3$)$_3$[56] and the one with Pt-H-Ag-H-Pt bridging in [(Et$_3$P)$_2$(Ar)Pt(μ-H)Ag(μ-H)Pt(Ar)(PEt$_3$)$_2$]$^+$ (Ar = C$_6$Cl$_5$) reported by Venanzi and coworkers[57a]. Also known are polynuclear complexes having μ_4 and μ_6 bridging hydrogen as in Mo$_4$(μ_4-H)(OCH$_2$Bu^t)$_{12}$ and Co$_6$(μ_6-H)(CO)$_{15}^-$[57b]. Some other typical hydrido complexes are MH$_4$(PPh$_3$)$_3$, MH$_2$(CO)(PPh$_3$)$_3$, MH$_2$(CO)(PPH$_3$)$_2$, etc.[58]. A large number of such transition metal hydrido conplexes are known which find considerable use as homogeneous catalysts in hydrogenation with the advantage of selective hydrogenation being possible with many such catalyst systems. Basolo and coworkers[59] demostrated (kinetically) a high trans-effect of H$^-$ ligand (this being sigma-trans-effect) comparable in terms of the trans-labilization with the pi-trans-effect of PR$_3$, being ca. 2×10^4 times stronger than that of Cl$^-$. The trans-labilization by H$^-$ is primarily due to stabilization of the five-coordinate transition state in ligand substitution in square-planar complexes of Pt^{II} rather than trans-bond weakening (trans-influence as it is called now)[60].

SnCl$_3^-$ is another strong trans-labilizing ligand which also forms typical complexes, mostly with platinum group of metals. Such complexes find use as homogeneous hydrogenation catalysts. A few examples of such complexes are Pt(SnCl$_3$)$_5^{3-}$, Pt(H)(SnCl$_3$)$_4^{3-}$, Pt(H)(SnCl$_3$)$_2$(PEt$_3$)$_2^-$, trans-Pt(H)(SnCl$_3$)(PEt$_3$)$_2$, cis- and trans-Pt(CO)(SnCl$_3$)Cl$_2^-$, RuCl$_2$(SnCl$_3$)$_4^{4-}$, Os(SnCl$_3$)$_6^{4-}$, etc.[61,62].

Many unusual oxidation states of metals have been stabilized, such as [Cr(bipy)$_3$]^n (n = –1, 0, +1, in addition to the usual +2 and +3)[63]. Authentic complexes of Au^{II}, both mono- and dinuclear, have been described[64], as also mono-, di- and tetranuclear complexes of Pt^{III}[65]; deep-blue

coloured [NBu$_4^t$][Pt(C$_6$Cl$_5$)$_4$] being the first example of a fully characterized mononuclear complex of Pt^{III}[65a]. Compounds of Tc in all the oxidation states from 0 to +7 have been reported[66]. A number of compounds of the halogens that were earlier considered non-existent have been isolated and studied, viz., KBrO$_4$ (stable up to 275°)[67] which in terms of $E^\circ_{BrO_4^-/BrO_3^-}$ = +1.76 V is a stronger oxidant than ClO$_4^-$ and IO$_4^-$, but at 25° it is only slowly reduced by Br$^-$ and I$^-$ and not at all by Cl$^-$ due to kinetic factors: HOF[68], FClO$_2$ and FNO$_2$[69] and a host of compounds having polyhalogen cations, X$_n^+$ (n = 2, 3, 5, 7) and X$_a$Y$_b^+$ (X and Y being two different halogens)[70]. Also of interest is the following thermal route for preparation of F$_2$[71] :

$$K_2MnF_6 + 2SbF_5 \xrightarrow{150°} 2KSbF_6 + MnF_3 + (1/2)F_2$$
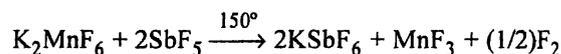
A European consortium has developed a new thermal method (Magnatherm process) for production (at 1550° in vacuum) of metallic magnesium that not only improved the existing process but which can also use hazardous asbestos waste alongwith dolomite or magnesite as a feed stock and bauxite as a flux to remove the SiO$_2$ formed in the reduction of MgO with Si of ferro-silicon used[72].

Since Alfred Stock's work on the boranes beginning in 1910, many additional boron hydrides have been prepared and studied. A total of 35 neutral binary boranes (including isomers) are known so far, the highest being B$_{20}$H$_{26}$ (7 isomers are known), this is a conjuncto borane, (B$_{10}$H$_{13}$)$_2$. Developments in metal and nonmetal cluster chemistry and non-classical carbocations owe much to the theoretical and structural studies of boranes, notably by W. N. Lipscomb and coworkers, for which Lipscomb was awarded (1976) the Nobel Prize in Chemistry. Many derivatives of boranes having organo and halo substituents have been synthesized and thousand other species have been generated via insertion of nonmetal and metal atoms into the borane framework forming heteroatomic frameworks, viz., carboranes, metalloboranes, metallocarboranes, etc. Icosahedral 1,2-C$_2$B$_{10}$H$_{12}$ can be converted to nido-C$_2$B$_9$H$_{11}^{2-}$ which forms η^5 sandwich compounds with metals analogous to those formed by Cp (Cp = C$_5$H$_5^-$), viz., Fe(C$_2$B$_9$H$_{11}$)$_2^{2-}$, Fe(C$_5$H$_5$)(C$_2$B$_9$H$_{11}$)$^-$, Fe(C$_5$H$_5$)(C$_2$B$_9$H$_{11}$), and also (C$_2$B$_9$H$_{11}$)Mn(CO)$_3$ analogous to (Cp)Mn(CO)$_3$. Auroboranes Au(B$_{10}$H$_{12}$)(B$_{10}$H$_{13}$)$^{2-}$ and Au(B$_{10}$H$_{12}$)$_2$ of sandwich structures have also been reported (Wynd and Welch, 1987), as also polyatomic species like (Cp)$_3$Co$_3$(B$_3$H$_5$), (Cp)$_4$Co$_4$-(B$_4$H$_4$), (Cp)$_4$Ni$_4$(B$_4$H$_4$), etc. The first report on boron clusters with B-F bonds appeared in 1996 (Ivabov et al.). For a review of carboranes and metalloboranes, and current activities on metalloboranes literature may be consulted[73].

Several metal cluster compounds derived from metal carbonyls and metal halides (of metals in low oxidation states) are known since many years. But during the last 30 years the literature in this field has grown profusely with several hundreds of new metal cluster compounds characterized, both of the homometallic and heterometallic types with or without other nonmetallic atoms (C, H, N, S, P) encapsulated within the polymetallic cage structure, and in these the nonmetallic atom shows many unusual coordination, e.g., η^6-C in $[Fe_6(CO)_{16}C]^{2-}$. It is hardly possible to make even a cursory mention of many of the salient developments in metal cluster chemistry in this article due to dearth of space. Hence, for this a literature survey is recommended, particularly the *Annual Reports on the Progress of Chemistry, Part A*, published by The Royal Society of Chemistry, U.K. and some authoritative reviews[74]. An interesting heterometallic superlarge cluster reported in 1996[75] is the giant anion $[Pd_{33}Ni_9(CO)_{41}(PPh_3)_6]^{4-}$, and several other giant species have also been reported, viz., $Au_{55}(PPh_3)_{12}Cl_6$, $Au_{22}Ag_{24}(PPh_3)_{12}Cl_{10}$, $[Pt_{38}(CO)_{44}H_x]^{2-}$, etc. Also of interest in this connection is the giant polymolybdate, $[Mo_{154}(NO)_{14}O_{420}(H_2O)_{70}]^{(25\pm5)-}$ of which the structure has been elucidated[76a], and two others, viz., $[Mo_{154}O_{448}(OH)_{14}(H_2O)_{70}]^{14-}$ of circular and $[Mo_{132}O_{372}(MeCO_2)_{30}(H_2O)_{72}]^{42-}$ of spherical topologies presented in a recently held international conference[76b]. Many of the metal carbonyl clusters are catalyst precursors of technological importance and are indeed widely used in various processes[77]. The interesting species $(Ag_5Br_8)_n^{2n-}$ has also been reported[78a] as also a wide range of metallocarbohedrenes[78b] which are robust clusters of general formulae M_8C_{12} (M = Ti, V, Cr, Fe, Zr, Mo, Hf) and $Ti_xM_yC_{12}$ (x + y = 8).

While $(Me_3PtI)_4$ was the first stable transition metal alkyl derivative to be prepared (Pope and Beachy, 1907), much of the developments in this area took place in later periods[79]. But most outstanding was the discovery of ferrocene[80a,b] having sandwich structure[80c], followed by a large number of compounds of this class[80d-f] of different metals and different such sandwiching ligands including the related $Cr(C_6H_6)_2$[81a] and also of multi-decker sandwich compounds[81b], and the one derived from alkali metal ions, $[M(Cp)_2]^+[S(NMe_2)_3]^-$ (M = Li, Na, K) reported by Wessel et al., in 1995[81c].

Since N. Bartlett's discovery (1962) of $Xe(PtF_6)_x$ (2 ⩾ x ⩾ 1) (actually the product obtained at 60° was later shown to be $(XeF)^+ (Pt_2F_{11})^-$) followed by preparation of XeF_4 by Classen et al. (1962) there has been very rapid advances in the chemistry of xenon compounds and many such have been prepared and characterized as also a few of Kr like KrF^+, $Kr_2F_3^+$ and $(F_3CCNKrF)^+$ stabilized by appropriate counter

anions, and KrF_2. KrF_2 is formed as a white solid on photolysis of a mixture of Kr and F_2 at $-196°$ and this decomposes at room temperature[82]. The discovery of stable xenon fluorides, XeF_2, XeF_4 and XeF_6 was a severe blow to the classical electronic theories of valence of Kossel, Lewis, Sidgwick and others. Interestingly, Pauling (1933) on theoretical considerations had predicted the likely existence of noble gas compounds, and Pimental (1951) expressed a similar view, but these were ignored because of the overwhelmingly prevalent classical ideas on valence. A host of compounds of Xe including the fluorides, oxyfluorides, oxides, and ionic species like XeF_5^+, $Xe_2F_{11}^+$, XeF_7^-, XeF_8^{2-}, $Xe_2F_{13}^-$, XeO_6^{4-}, etc., have been prepared and structures of many of these have been determined[83].

Of considerable interest in xenon chemistry are species with Xe-C and Xe-N bonds[84a-f], viz. $[Xe(2,6-C_6H_3F_2)]^+$-$(BF_4)^-$, $[Xe(C_6F_5)]^+(AsF_6)^-$, $[Xe(C_6F_{11})]^+ (AsF_6)^-$, $Xe(N(SO_2F)_2)_2$, $[XeN(SO_2F)_2]^+(AsF_6)^-$, $F(XeN(SO_2F)_2^+)_2$-$(AsF_6)^-$, etc. An extension of xenon chemistry is the formation of species with Xe-Xe bond, viz. $(Xe_2)^+(Sb_4F_{21})^-$ with a Xe-Xe bond length of 3.087 Å (Re-Re in $Re_2(CO)_{10}$ is 3.041 Å) being the longest known bond so far[84g]. Spectroscopic evidence has been furnished for $[Kr-H-Kr]^+$, $[Xe-H-Xe]^+$, $[H-Kr]^+$ and $[H-Xe]^+$[84h], and also XeH_2[84i].

The chemistry of S-N compounds continues to attract attention for various reasons, one being their interesting electrical properties (high electrical conductivity of some such compounds), and complexes formed by S-N chelating ligands, viz. S_3N^-, S_7N^-, $S_2N_2^-$, etc., have been reviewed[85]. Ring forming abilities of elements other than carbon have often been underestimated. While species like S_8^{2-}, $(NPCl_2)_x$ and S_4N_4 are known since earlier times, in the 1990s we did witness the syntheses of a wide variety of species of both homonuclear and heteronuclear rings, such as S_4^{2+}, S_8^{2+}, S_{19}^{2+}, Se_4^{2+}, Te_8^{2-}, Te_8^{2+}, $Si_2S_6Cl_2^{2-}$, Br_2TeSeN_2S, $As_2S_6^{2-}$, $(B_3S_6)^{3-}$, $S_4N_5^-$, $S_5N_5^+$, S_7NH, S_8NH, etc. (*cf. Chem. Brit.*, April, 1997 and February, 1998). In $(SN)_x$ we see a variety of ring, cage and chain structures, but what is of utmost interest is the discovery of superconducting properties of several such compounds (*cf. Chem. Brit.*, April, 1997).

Isolation and characterization of carbon cage clusters, the fullerenes, such as C_{60}, C_{70} and many others up to C_{600} reported so far and elucidation of their structures[86a] are some of the most significant developments. C_{60} has been shown (1990) to have the shape of a soccer ball (bucky-ball), while C_{70} has the shape of a rugby ball; C_{120} has a dumb-bell shaped structure of two C_{60} units linked through four C-C bonds, and similar dumb-bell shaped species having two C_{60} linked through some O or S bridging groups also are known and are named bucky-bells[86b]. All the fullerenes from

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C_{40} and above have an even number of carbon atoms, but in clusters upto C_{25} both odd and even numbers of carbon atoms have been observed. A chiral C_{76} has been resolved (1993). The higher members have tubular structures[87]. Alkali fullerides have been prepared which have M^+ incorporated within the cage, as in M_3C_{60}, M_4C_{60} and M_6C_{60}. Interestingly, while M_4C_{60} is an insulator, M_3C_{60} exhibits superconductivity (T_c = 18 K for K_3C_{60}; T_c increases with increase in size of M^+)[88a-c]. Other metals can also be incorporated to form species such as La_3C_{60} having La^{III} ions. Chemistry of fullerenes has been reviewed[88d].

On treatment with Zn and conc. HCl, C_{60} and C_{70} form $C_{60}H_{36}$ and $C_{70}H_{36/38}$, and more fully hydrogenated species are also formed[89]. Interest in fullerene cycloaddition chemistry[90] continues that has led to the preparation of several metal complex-fullerene adducts. Another interesting reaction of C_{60} is[91a],

$$C_{60} \xrightarrow[\text{Toluene/2,2,2-crypt}]{\text{DMF/K}} [K(2,2,2\text{-crypt})]_2^+ \ (C_{60})^{2-}$$
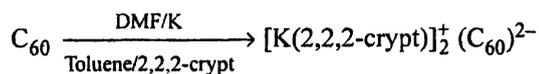
Fluorination of C_{60} by F_2 gives $C_{60}F_{48}$ and $C_{60}F_{60}$[91b,c]. $C_{60}F_{44}$ and $C_{60}F_{78}$ have been reported as products of reaction of C_{60} with KrF_2[91d]. For several interesting reactions of fullerenes the original literature be consulted[92a-d]. Also of interest are the so-called inorganic fullerenes[92e] formed by MS_2 and MSe_2 of M = Mo, W. Many transition metal sulfides and selenides can form fullerene like materials including the large nanotubes in a way similar to carbon[93]. Similar behaviour has been reported[94] in $(NiCl_2)_x$.

Magnets play a crucial role in the development of modern society and there is a continuing search for new magnetic materials. Magnetic materials made of Mn complexes of porphyrin derivatives have been made (1992) which have promising use in a variety of devices of our every day life (*Chem. Brit.*, June, 1994). Silanes with a range of functional groups are now known to be far superior than conventional agents for coating metal surfaces. This new technology avoids many of the environmentally undesirable chromate and phosphate processes (*Chem. Brit.*, January, 1998). WS_2 based bucky-balls provide a promising alternative to traditional machine lubricants, being six times more effective in cutting down wear and tear of machine parts than the best conventional MoO_3. Its first synthesis was reported in 1992 and improved synthesis reported in 1997 (*Chem. Brit.*, September, 1997; *Nature*, June 19, 1997). Silicone based adhesives such as $(Me_2Si(OH)_2)_x$ (gums or fluids depending on x value) for transdermal drug delivery (controlled release of drug from a patch applied to the skin with a suitable adhesive) since 1990s have been prepared and preferred

due to their biocompatibility (*Chem. Brit.*, January, 1991).

Polyaluminosilicate-sulfate, developed independently in Canada and in U.K., as a coagulant for water treatment need less pH control and much lower dose to achieve the equivalent performance of alum. Polyferric sulfate is even better than conventional coagulants for removing particulates including algal materials and natural organic matter from surface waters. Two mixed Al-Fe coagulants, polyaluminoferric sulfate (1997) and ferral (1997) are attracting much attention. Ferral is made from waste product from clay processing which was developed in the U.K. and received the Queen's award in 1997 for environmental achievement. Their properties and performance depend on Al : Fe and metal : OH ratios (*Chem. Brit.*, March, 1999).

Of late there is a continuing search for inorganic flame retardants for use in place of conventional organohalogen and organophosphonium compounds. It is envisaged that by the year 2003 purely inorganic flame retardants will contribute *ca.* 36% of the world use in terms of revenue (vide "Conference on Flame Retardants" held in 1998, *Chem. Brit.*, June, 1998). These are of greater preference because of non-generation of asphyxiant gases (CO_2, CO, HCN, etc.), organic irritants (acrolein, crotonaldehyde, formaldehyde, phenol, styrene, etc.) and inorganic irritants (HX, X = halogen, NO_x, SO_2 or phosphates). Inorganic flame retardants of some common use are $Al(OH)_3$, $Mg(OH)_2$, Sb_2O_3, zinc borate, zinc stannate, zinc hydroxystannate, etc., in suitable mixtures or singly.

The developments since 1992 of glasses doped with Ln^{3+} is driving optical fibres into an expanding range of important, useful and surprising applications (*Chem. Brit.*, May, 1997). Lanthanon based fluorescence sensors have been developed which help to monitor change in pH of cellular body fluids in patients in medical IC units that helps to provide vital early warning of an imminent cardiac arrest and thus helps to provide medical staff precious time to intervene before any damage is done (*Chem. Brit.*, December, 1996).

Catalysis occupies a pivotal position in the chemical industry. Detailed information about catalyst structures and activities obtained by imaging catalyst surfaces *in situ* is already allowing researchers to start rationally designing new and improved catalysts (*Chem. Brit.*, June, 1997). In 1995, researchers at York University, U.K., developed a range of supported catalysts (called *Envirocats*, being environmentally friendly) which demonstrate significant advantages over traditional catalysts in terms of processing efficiency, higher selectivity, health safety and environment protection. These can be used for the synthesis of a range of organic interme-

diates for the pharmaceutical, agrochemical and related industries. Envirocats can be used with success in place of traditional catalysts like anhydrous $AlCl_3$ in Friedel-Crafts reaction. Some 40 years after the introduction (1952) of the Ziegler-Natta catalysts for polymerization of olefins there began revolutionary changes in the 1990s due to introduction of metallocenes as catalysts. Highly active metallocene catalysts enable tailor-made polymers to be synthesized, they are 10-100 times more active than the traditional Ziegler-Natta catalysts[95a]. Scientists at Hamburg University in Germany discovered (1977) that metallocenes, particularly $(Cp)_2ZrCl_2$, in combination with methyl-aluminooxane $(Al_4O_3Me_6)_x$ clusters, formed by the controlled hydrolysis of Me_3Al, enhances the catalytic activity by a factor of ca. 10^4 as compared to metallocene + Al-alkyl catalyst systems. Metallocene catalysts enable the polymer chemists to obtain the goals that have never been possible before with the traditional heterogeneous Ziegler-Natta catalysts. Their biggest impact will be in the synthesis of elastomers and it is predicted that by the end of the year 2000, metallocenes would capture as much as 75% of the elastomer market in Western Europe (Chem Brit., February, 1998). An area where metallocene polymers like metallocene-polyethylenes are already making a headway is in the film packaging industry. Fruits like bananas packed in such materials stay fresh without refrigeration for long periods because these films are impervious to water and moisture. In USA such packaging materials are marketed since 1991 and further improvements took place in 1996. Many such developments have opened up new frontiers in organometallic chemistry and polymer synthesis. Chemists are also using designer zeolites to create a new class of enzyme mimics for synthesising chiral drugs and agrochemicals (Chem Brit., July, 1997). Also worth reporting in this connection, the cases of so-called 'Magic Catalysts'[95b] which are interstitial carbides and nitrides of Mo and W. Their activities are comparable to some of the best traditional platinum group metals but are much cheaper and hence more economical. Both WC and Mo_2C are useful in the following types of reactions : (a) Fischer-Tropsch process and alcohol synthesis, (b) methane reforming by reaction of CH_4 with $O_2/H_2O/CO_2$ to produce $CO + H_2$, (c) reaction of C_4H_4S with H_2 forming open straight-chain $C_4H_{10} + H_2S$, (d) cracking of petroleum to produce light hydrocarbons, and (e) isomerization (straight-chain to branched chain product) for making high octane fuel. Similarly, W_2N and Mo_2N are useful for (a) conversion of $N_2 + H_2$ to NH_3 and (b) converting C_5H_5N by reacting with H_2 forming straight chain $C_5H_{12} + NH_3$. Some of the above reactions are of much use in the oil industry.

Jacobson et al., have found several new active and stable catalysts that produce NH_3 under industrially relevant conditions. These are M_2MoN (M = Fe, Co). At a pressure of 50 bar and 400° the ternary nitride catalysts are more than twice as active compared to the traditional iron based (Os or Ru promoted) catalyst used in the Haber process. It is estimated that ca. 1% of world energy usage is expended in the production of NH_3. Hence, even a small improvent in efficiency could have significant impact on fossil fuel consumption and consequently on emission reduction (Chem Brit., August, 2000).

Superconductivity was first discovered by Onnes (1911) in metallic mercury cooled to 4.2 K. The next 50 years witnessed newer materials showing superconducting properties at relatively higher temperatures, and the material Nb_3Ge with $T_c = 23.7$ K was the best known till 1973 and a cheaper Nb-Sn alloy was also known having $T_c = 22$ K. Such materials were used in magnetic windings of powerful electromagnets having major applications in NMR, in particle accelerators and similar devices. Unfortunately, the low temperature needed to achieve superconductivity required use of expensive liquid He as coolant and hence large-scale commercial applications such as for power transmission were out of question. Hence, there was a continued search for materials with higher T_c. In 1986, Bednorz and Muller[96] in Switzerland announced a mixed oxide of metals ultimately formulated as $La_{2-x}Ba_xCuO_{4-y}$ (where $x = 0.15$–0.2, and y is undefined but small) which was superconducting with a T_c of 35 K. This created enormous interest and reports of newer materials with higher T_c poured out of the U.S.A., Japan, China and other countries of the world. In 1987, Chu et al., reported $YBa_2Cu_3O_{7-x}$ which is superconducting when $x \approx 0.1$ but semiconducting when $X \gtrsim 0.5$ and its T_c is 93 K. Replacement of Y by Ho, Sm, Eu, Dy and Yb also gave materials with T_c around 90 K. The greatest advantage is that T_c is above the boiling point (77 K) of liquid nitrogen and hence superconductivity could be achieved more cheaply using liquid nitrogen as the coolent instead of the expensive liquid helium. Early in 1988, two new systems having Bi or Tl in place of the lanthanides were reported with T_c around 122 K, such as for $Tl_2Ba_2Ca_2Cu_3O_{10}$, $TlBa_2Ca_3Cu_4O_{11}$ and $(Tl, Pb)Sr_2Ca_2Cu_3O_9$[97]. These are also much less brittle which should make fabrication easier. Superconductivity in metallic tellurides has also been reported[98].

Geomimetic chemistry developed during the last 40 years is another promising area of research where the aim is to synthesize rocks and minerals of natural occurrence and other similar materials which do not occur in nature but which

have properties suitable for important large-scale commercial applications as well as for aesthetic reasons for use in arts and crafts. A knowledge of the structural features and compositions of the natural compounds has enabled considerable advances in this area. With over 3500 known mineral species, we have a lot of such materials to synthesize not only to mimic the natural substances, but also to improve and enhance their properties for a variety of applications, viz., as ion-exchangers, as catalysts and catalyst support, adsorption and separation of gases in molecular sieves and in gas chromatography, as pigments of high thermal and chemical stability for use in ceramics, fluorescers as lasers, as ferro-electric and ferro-magnetic materials in magnetic storage devices, as also as gems in jewellery. These include not only those similar to the natural materials such as the zeolites (about 200 varieties have been synthesized of which only 80 occur in nature), ultramarines such as (Lapis Lazuli), spinels, boracite, sodalite, etc., but also a variety of similar materials having a wide range of other elements in place of the natural constituents of the well-known minerals. Using the structure of a single naturally occurring mineral as a blue-print, inorganic chemists can exploit the diversity of the Periodic Table to design new materials of endless varieties in their physical and chemical properties which can be of ample benefit to chemists, physicists and technologists. A few such examples are $M_8\{GaGeO_4\}_6X_2$ (X^-= halide, S_3^-, perchlorate, permanganate) of the sodalite family, $Ca_8\{Ga_2SiO_6\}_4(OH)_8$ of the zeolite family reported in 1995, ultramarines having yellow chromate in place of the blue chromophore S_3^-, cobalt green, (Co, Ni, Zn)-$(Ti,Al)_2O_4$, and spinel black, $Cu(Cr,Fe)_2O_4$, both of the spinel class, etc., in addition to the known minerals like Lapis Lazuli, $Na_8(SiAlO_4)_6(S_3,S_3)_2$, spinel, $MgAl_2O_4$, Egyptian blue, $CaCuSi_4O_{10}$, etc. There are many natural ones which could not be synthesized so far, an imortant example being *clinoptilolite* of the zeolite family which is much in demand in nuclear industry to decontaminate spent effluent of nuclear piles because of its natural affinity for Cs^+ and Sr^{2+}. All attempts to make this synthetically have failed so far and hence further attempts are needed. But megatonnes of Zeolite-A and Zeolite-P (developed in 1997) are much in use as water softners in washing powders and these have almost totally replaced the environmentally damaging polyphosphates used previously. A synthetic zeolite ZSM-5, $Na_3(AlSi_{31}O_{64})_3.16H_2O$, is used to produce gasoline from methanol on a large scale in some countries without natural petroleum. Synthetic zeolites of desired channel size are of much use as catalysts or catalyst support, as water softeners, as molecular sieves[99]. The shape-size selectivity is illustrated by the synthesis of *p*-xylene in preference to the

unwanted usual *o*-xylene . The rod-shaped *p*-xylene molecules fit into the pores of ZSM-5, but the *o*-xylene molecules do not.

Destruction of NO_x in flue gases by selective catalytic reduction with NH_3 is in use since 1970s. The most common catalysts are TiO_2 and V_2O_5. Generally a mixture of the two with a little WO_3 is used impregnated onto metallic or ceramic surfaces, operate at 200–400° (over 90% reduction occus at *ca.* 350°). A 1 : 1 or less $NH_3 : NO_x$ is used to minimise NH_3 emission. More recently, a zeolite molecular sieve catalyst has been developed for higher temperature (350–600°) applications. The properties of zeolites can be altered to improve their NO_x reduction activity by heat treatment changing the $SiO_2 : Al_2O_3$ ratio, and adding various metals onto the zeolite. Noble metal catalysts based on Pd, Pt have been developed for low temperature (170–300°) use. Reduction of NO_x on a carbon bed impregnated with Cu or Ag forming $CO_2 + N_2$ is another recent finding which works even at 150°, but efficiency is *ca.* 11% only (*Chem Brit*, March, 1998).

In the present day energy scenario with a gloomy future there is considerable interest for the production of H_2 for use as a fuel by water-splitting in a photochemical process in presence of metal compounds or complexes as photocatalysts. A few such systems have been reported and further work to achieve greater efficiency for practical use is of much promise. The most effective systems reported so far are based on $Ru(bipy)_3^{2+}$ type complexes as photocatalysts[100]. Equally important alongwith this is a method for storage and easy transportation of the generated H_2. In this regard $LaNi_5H_6$ (which has more H_2 per unit volume than liquid H_2) is promising. $FeTiH_x$ ($x \approx 1.95$) has already been tested in trial runs as a source of fuel in vehicles. A lead incorporated $KNbO_3$ catalyses H_2O splitting in visible light (sunlight); in presence of MeOH in the water only H_2 is evolved, but in presence of dissolved $AgNO_3$ only O_2 is liberated (Japanese patent, 1992).Various types of fuel cells for production of electricity have been described some of which can use $H_2 + CO$ (from steam reforming of CH_4 from natural gas) or even a hydrocarbon, like *n*-butane, directly (*Chem Brit* , June, 2000).

Uses of metal complexes as catalysts in electrochemical processes for conversion of environmentally undesirable species in water into harmless substances or for their elimination have been described and much more work in this area appears promising.

Decontamination of foodstaff from insecticide and pesticide residues is a serious challenge. The present world population is *ca.* 5.5 billion; with a growth rate of *ca.* 0.24

million people each day the population would be *ca.* 15 billion by 2100 A.D. Some 1.5 billion people today are malnourished. About 98% of the food comes from agricultural land and terrestrial ecosystems. Nearly 35% of the total crops are lost due to pests, insects, etc., despite wide application of *ca.* 2.5 million tons of pesticides annually worldover, although less than 1/3rd of agricultural crop land worldover is treated with pesticides. Annually, *ca.* 0.5 million accidental human poisoning and 10000 deaths occur worldwide from pesticide contaminants in foods and drinking water, and the percentage is the greatest in developing countries. The percentage is the least in U.S.A. where US $ 1200 million is spent annually for monitoring wells and ground-water for pesticide contamination. There are other unrecorded losses due to loss of aquatic life forms, destruction of invertibrates and microbes in soil, health problems due to contaminated food, etc. (*Chem Brit* , July, 1999). It is therefore essential to make a hot pursuit to develop materials that are easily biodegradable leading to harmless products. The chemical reactivities and biochemical activities of substrates are known to be drastically altered by complexation with metal ions. Hence, metal incorporation in pesticides, many of which have potential metal binding sites, may increase their potency, so that less of the material would be needed, and accelerate its biodegradability in nature and this may be exploited with success. It is worthnoting in this connection that several metal containing insecticides and pesticides are already in use. Much more research is needed in this area of promise.

Considerable advances have taken place in bioinorganic chemistry during the last half a century. In 1940 carbonic anhydrase was shown to be a Zn-enzyme, and in 1955 carboxypeptidase became the second recognised Zn-enzyme and its structure was elucidated by Lipscomb in 1972. Since then about 300 Zn-enzymes have been reported and the structures of 20 of these are already known[101]. Technically these are of various kinds including the DNA and RNA polymerases. There has been a profuse growth of literature in the elucidation of the roles of many metalloenzymes and their structural features, and making model compounds mimicking the metalloenzymes. But few such ideal models have been made so far that mimic both the structural features of the active sites of the metalloenzyme (i.e., metal and its coordination environment) and its catalytic property. However, many models have been made that represent either of the above features which have lead to considerable advances in our understanding the role of metal ions in biological systems and in bioinorganic chemistry during the last 30 years. Picket-fence iron-porphyrin reported by Collman and coworkers in 1977 was the first ideal struc-

tural and functional model for hemoglobin. Several metal complexes have been studied as functional models of several enzymes like ascorbate oxidase (Martell, 1967), amine oxidase (Hamilton and Revesz, 1966), peroxidases (Martell *et al.*, 1972), carbonic anhydrase (Kimura *et al.*, 1990), etc. Several reports appeared in 1986 and subsequently on dinuclear Cu complexes as models of multicopper enzymes like non-blue and blue copper proteins, of hemocyanins, catalases, Cu/Zn superoxide dismutase, galactose oxidase, etc.[102]. Copper complexes of binucleating ligands which provide Cu_2^I-models for hemocyanin and tyrosinase and other Cu-enzymes have been described[103]. Model compounds mimicing hemoglobin and myoglobin[104], cytochromes[105] and multidentate non-porphyrin ligand complexes of Fe^{II} modeling non-heme proteins[106] have been described. Fe-S complexes have been studied extensively because of their relationship to non-heme Fe-S proteins and a large number of synthetic species $Fe_xS_y(SR)_z^{n-}$ are known as structural and functional models of the Fe_4S_4 type units present in many enzymes[107]. A prime feature of these systems like $Fe(SR)_4^{n-}$, $Fe_4S_4(SR)_4^{n-}$ ($n = 1–4$) is reversible electron transfer redox reactions which provide a clue to the importance of such polymer species in natural enzymes. A series of Mo-Fe-S clusters, all of which contain two basic cubane structures made up of Fe_3MoS_4 units linked together by a variety of bridging modes, have been prepared and studied[108]. Mössbauer data on the Fe indicated a similar oxidation state to that found in the Fe-Mo co-factor of nitrogenase. One of the compounds having two $(EtSFe)_3MoS_4$ units linked through the Mo atoms by two SEt and one S as bridging groups, by EXAFS criterion, most closely resembles the Mo environment in the Fe-Mo co-factor of nitrogenase. Other important publications on models for ferredoxin[109] and nitrogenases[110] have appeared. Since 1983 there appeared many interesting publications on compounds of Mn that might provide models for, or at least provide some insight into, the role of Mn in photosynthesis and in several enzyme systems containing Mn^{III}. It appears that tetranuclear Mn complexes are involved in photosynthesis that undergo oxidation/reduction cycles in photosystem II where the overall reaction is $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$. It is of interest to note in this connection that the dinuclear Mn^{III} complex, $(Mn(salen)(H_2O))_2^{2+}$ (salen = 3,5-dichlorosalicylidine-1,2-diaminoethane) on photolysis with visible light produces O_2[112]. Polynuclear Fe^{III} complexes having oxo and hydroxo/methoxo ligands have been reported that serve as models for ferritin[113]. Imidazole and *p*-nitrophenolate complexes of oxo-Fe^{IV}-porphyrin pi-cation radicals have been described[114a] as models for compound I, the intermediate identified in the catalytic cycles of peroxidase, catalase, etc.

Two novel dinuclear complexes of Mg have been described which serve as models for active sites of dimetallic hydrolases[114b] and a dinuclear Fe complex as hemerythrin model[114c]. Many such studies of models of biomolecules has led to emergence of what is now known as *biomimetic chemistry*. At the recently held 34th International Conference on Coordination Chemistry at Edinburgh (July, 2000), several works were presented on studies of several such model compounds/systems (vide Abstract nos. 1053,1074, 1083,1086,1103,1114, 1118, 1132 in particular).

Recognition of the physiological role of NO is a significant development in bioinorganic chemistry[115]. The hypotensive effects of hydroxamic acids may be due to their ability to release NO, while many of their ubiquitous role in biology and medicine is surely due to their ability for chelating metal ions[116]. NO is produced in the brain as a messenger molecule of neurons and NO serves as a neurotransmitter in penile erection. Its function is presumably related to its role as a physiological mediator of blood vessel relaxation. Erectile disfunction in male is now known to be due to lack of release of NO due to disorder in metabolic function.

During the last 50 years considerable advances have been made in the field of mechanisms of inorganic reactions. Despite a few such studies reported earlier this remained a neglected field as would be quite revealing from what Fred Basolo narrated in an interview[117]. In the year 1955 Fred after listening to a lecture by W. Hieber on some of his fascinating contributions in the field of synthesis and reactions of metal carbonyls, which he reported in the lecture which he delivered at the International Conference on Coordination Chemistry at Amsterdam (May, 1955), asked Professor Hieber if he had any idea as to how the nice and novel types of substitutions on metal carbonyls could take place. To this Professor Hieber looked at Fred and said "young man, in my laboratory we do real chemistry, we don't do philosophy of chemistry". The position has of course changed dramatically since then and for this much of the credit is due to Professor Fred Basolo for the outstanding contributions of his group, mostly in collaboration with Professor Ralph G. Pearson, at Northwestern University, Evanston, Il., U.S.A. Many other centres of excellence in the field grew up in the later periods in different parts of the world. The present author had the privilege to be initiated into this fascinating field from his association with Fred Basolo and Ralph G. Pearson in 1956. It is significant to note that at the recently held 34-ICCC at Edinburgh a fairly large number (68) of invited presentations were made in the section on Structure and Dynamics of this conference. In the last decade of the 20th century the number of publications in the field of inor-

ganic reaction mechanisms constituted *ca.* 15% of the total number of publications in all branches of inorganic chemistry. A new international journal *Inorganic Reaction Mechanisms* is being published since 1999. With the advent of techniques for following fast reactions and determining volumes of activation, there has been a considerable widening of the scope of activities in this field since the late sixties. Various criteria have been used to diagnose the plausible mechanisms and to infer about the reaction courses for various types and classes of reactions[118]. Kinetic studies on formation and dissociation of ternary complexes have helped much to arrive at stability-lability correlation for such systems and obtain information of significance in elecidation of the role of metal ions biological systems[119]. Complexation by multidentate ligands has remarkable features and more so for macrocyclic ligands. A recent example being metal ion incorporation in a porphyrin derivative[120a]. Novel features have been observed in the complexation of some transition metal ions with a quadridentate ligand providing N_2S_2 coordination[120b]. Two well-known intramolecular twist mechanisms for racemization of metal complexes had been proposed, viz., Ray-Dutt twist (1943)and Bailar twist (1958). Experimental demostration of the validity of either of the mechanisms is not easy. However, Bailar and coworkers[121] reported that in the solid state at *ca.* 160° *cis-α*-[Co(trien)Cl$_2$]Cl undergoes slow isomerization to the *cis-β*-isomer which could be rationalized only by the operation of the tetragonal twist (Bailar twist). In the solid state at temperatures well below 200° the complexes *l-cis*-[M(en)$_2$Cl$_2$]Cl (M = Co, Cr) undergo racemization at slow but measurable rates without any *cis-trans* interconversion. This could only be rationalized by the operatiaon of rhombic (Ray-Dutt) twist[122]. On the basis of theoretical calculations, Rodger and Johnson[123] concluded that Bailar twist should be favoured for chelating ligands with a small bite distance compared to the L–L distance of the donor atoms (L) of the chelating ligand bonded to the metal. Henry Taube was awarded the Nobel Prize in Chemistry (1983) for his contributions in the field of mechanistic aspects of redox/electron transfer reactions[124].

Applications of metal complexes and organometallic compounds as catalysts (both in laboratory and technological processes), in medical diagnosis, in medicine, in trace analysis, etc., have been well exploited and are likely to progress more in the near future. In connection with trace analysis, uses of complexes in kinetic methods of trace analysis have led to developments of methods that can be used to monitor some of the polluting metals of much environmental concern even at the ppb level (as with Hg, Pb, Cr, etc.). Biomimetic chemistry is another area where a lot more is

yet to be achieved, particularly in making models that truly represent the active sites of metalloenzymes both in their structural and reactivity features. Coordination chemistry has a great promise in the monitoring, abatement and control of environmental pollution. All such diverse activities in the coming years is surely going to make significant advances of our knowledge and understanding of the chemistry of elements *in vitro* and *in vivo*.

Concluding remarks

Good research is painstaking. In 1907, Urbain separated Yb from Lu by fractional crystallization of their salts repeated 15000 times, as the presently available sophisticated techniques like ion-exchange were not available then. In 1898, the Curies succeeded in separating a few mg of $RaSO_4$ from a few tons of pitchblende mineral. Structure of Vitamin-B_{12} was solved (1956) by Hodgkin after 35 years of work with X-ray analysis, structure of hemoglobin was solved (1960) by Perutz after more then 20 years of work in X-ray analysis. These are just a few examples. However, for good work, apart from congenial atmosphere, generous funding is of utmost necessity for research in chemistry in recent times, and a better appreciation for basic science. In the words of (late) Professor Joseph Chatt[125], one of the outstanding inorganic chemists of the 20th century, "Until now scientists spend almost as much, if not more, time foraging for the money to support their work than they do in creative science. The legislators talk of relevance, but the most important discoveries of science were rarely planned... .... and the scientist who discovers it may never know the value and extent of what he has found. A prime example is Kippling's discovery of silicones".

The Indian Chemical Society ought to play a role similar to that of the Royal Society of Chemistry in the U.K., and the ACS in the U.S.A. for close monitoring and making recommendations for updating the teaching and research in chemistry in the Indian Universities. The syllabi and prescribed courses followed and the methods of teaching and evaluation in our Universities are so much outdated as to require a drastic change. Even the so-called revisions carried out in recent years in some of our supposed to be the leading Indian Universities have indeed made the situation no better in most cases; the revisions proposed are lacking coherency and consistency needed for a systematic build-up of usable knowledge and enthuse young minds to acquire the knowledge. To those engaged in teaching the author would like to suggest with all humility that they read the article "Fifty-six Laws of Good Teaching" published in the *Jounal of Chemical Education* in May, 1990 issue. The

utility of class room demonstrations cannot be over emphasized to make chemistry teaching exciting. There are a number of simple and easy to perform experiments suitable for lecture demostrations and several sources are available[126] for one to make a choice according to his needs. It is most unfortunate that for various reasons, which I wish not to spell out to avoid any controversy, the teaching profession is no longer attracting the best available talents in the country. We do need men like Asutosh Mookerjee and Prafulla Chandra Ray to bring a reversal of this trend.

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