

INAUGURAL LECTURE SERIES

15



**LADOKE AKINTOLA  
UNIVERSITY OF TECHNOLOGY  
OGBOMOSO, NIGERIA**

**MOLECULAR ARCHITECTURE:  
Juggling Metals and Electrons  
for Technological Advancement**



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**Professor Olusegun A. ODUNOLA**

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**MOLECULAR ARCHITECTURE:**

*Juggling Metals and Electrons for Technological Advancement*

**INAUGURAL LECTURE SERIES 15**

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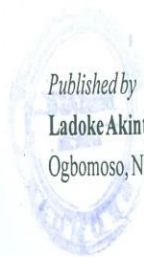
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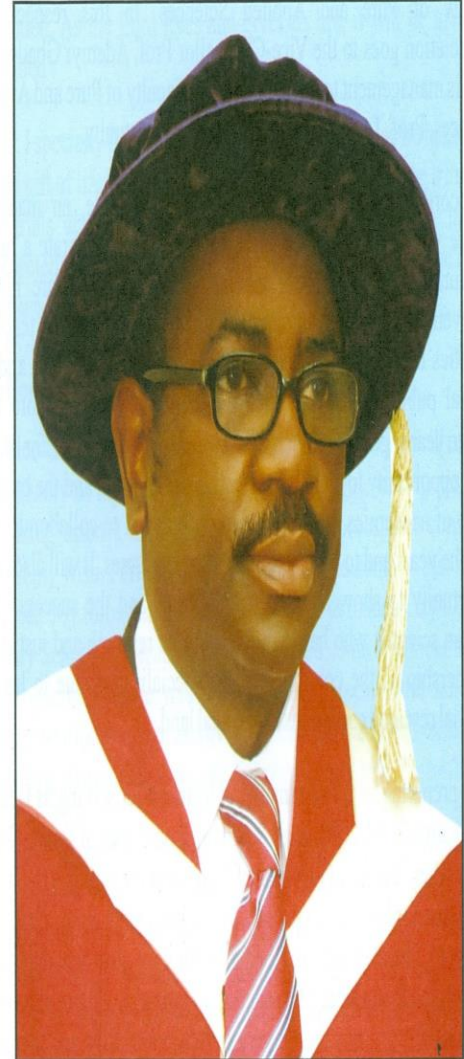
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## **MOLECULAR ARCHITECTURE: *Juggling Metals and Electrons for Technological Advancement***

### **Preamble**

It is indeed, a great honour and privilege for me to give the fifteenth inaugural lecture of this great University and the fourth from the Faculty of Pure and Applied Sciences. In this respect, my appreciation goes to the Vice-Chancellor Prof. Adeniyi Gbadegesin and his management team and the Dean, Faculty of Pure and Applied Sciences, Prof. Temidayo Ayodele for this opportunity.

In accordance with academic tradition worldwide, an inaugural lecture within a University is an opportunity to celebrate a newly inaugurated Professor. The scholar is expected to share his/her achievements in research, innovation, engagements and teaching activities before an audience of members of the University and the general public. However, since I became a Professor more than sixteen years ago (1<sup>st</sup> October, 1999); this inaugural lecture for me is a great opportunity to thank my current research team and the brilliant group of academics that I have been privileged to collaborate with over the years and to celebrate our shared successes. It will also be an opportunity to showcase the travails, trials and the success of an African scientist who has to globetrot to do research and justify his membership of the commune of his specialization due to lack of minimal research conditions in his natal land.

I was preparing to give an Inaugural lecture after serving as Dean of my Faculty (2004-2008) and Chairman, Committee of Deans (2006-2008) when the then Governor of Oyo State in April 2010, Otunba (Dr.) Christopher Adebayo Alao-Akala graciously appointed me as Rector of The Polytechnic, Ibadan, with very clear mandate to re-position the Institution. The arduous assignment without any iota of doubt left little or no time for very serious preparation and focus that an epoch and profound event of inaugural lecture requires. I remain grateful to him for the opportunity to serve Oyo State and the Nation in that capacity. Early in 2015, I felt honoured and elated when the Dean of my Faculty, a respectable gentle man with a good heart, Prof. E. T. Ayodele requested that I should give an inaugural lecture on behalf of the Faculty. Two months later, I was appointed foundation Vice-Chancellor of Hallmark University. Then, he came to congratulate me and rejoiced with me and the next question was, 'Sir, what happens to the Faculty's inaugural lecture? To which I responded, As the Lord lives and gives us life, it will be given as scheduled'.

Today, I specially thank God Almighty for this is the day he has made, for the gift of life, sustenance, providence, good health and triumphs over trials and treachery in this journey of life so far, largely unexpected but nevertheless magnificent. Honour and glory be to His holy name.

## **The Beginning**

Mr. Vice-Chancellor sir, permit me to begin this lecture with a very brief history of my early years and initial struggle or reluctance of embracing science as a discipline and the forces that conspired against my wish. Perhaps, this might minister to some in this mixed audience. My formal education which started at Ibadan City Council Primary School, Beyerunka, Ibadan, in 1968 some few meters from my progenitor's castle was very exciting. I recall with nostalgia sharing the trips to school and evening lesson in the good company of my darling sister and first 'mentee' Oluyinka (now Mrs. Akinsola).

Mr. Vice-Chancellor, something remarkable happened in the third term of primary three. During the period, my mother- a teacher felt I had been too playful and may not perform well to be able to receive end of year prizes and commendation at the end of the term. Having led the three arms of my class the first two terms, my young mind felt it was not possible. As she rightly predicted, I came second but received prizes. However, I gave the prizes to some classmates who failed to console them. On getting home she wasn't very pleased with my report card but I gleefully told her about what happened in school. She allowed me to finish my lunch and gave me a very nice flogging that still resonates vividly today, 45 years after.

Secondary school was even more interesting. I was privileged to spend the formative period of my educational career at Lagelu Grammar School, Ibadan in the company of the most brilliant boys that can ever be assembled. This was an Institution where leaders were groomed, careers shaped and the future assured. The school was also blessed with very dedicated teachers and principals who contributed significantly to our receiving holistic education that was able to prepare us for leadership at young age. However from early 1976, the school greatly suffered hemorrhage of its finest teachers in many subjects, worse hit were the sciences. The benefactors of the 'brain drains' were mainly the 'local ivy schools' in Ibadan.

Mr. Vice-Chancellor, if my encounter in primary school was my mother, I never realized my father was waiting for me. Here is an Economist, Theologian and graduate of Business Administration who was teaching virtually every subject. Our initial teacher student relationship ended abruptly when my inability to answer a simple question on quadratic equation in 1974 met with a gentle slap, the only time he ever disciplined me corporally. He thereafter arranged a private tutor for me during that vacation. In my penultimate year in secondary school, he asked what career I would like to pursue with average grades in the sciences, best student in economics and good results in English language, and literature. I answered with what I considered a flawless argument; with lack of adequate and stable teachers in the sciences I would like to study law or social sciences. He gave me a very

meaningful glance and 'ordered'; you must read sciences. Why the man wanted his son to be a scientist, only he could probably answer because I never bothered to ask.

No doubt, these two experiences with my biological parents laid the foundation for my foray into sciences, otherwise if today would come at all; I probably would have been giving an inaugural lecture on law, economics or psychology, disciplines that I then well-liked outside the sciences.

Alas, I became free from direct parental influences after gaining admission to University of Ife (Unife) now Obafemi Awolowo University, where I graduated with Bachelors of Science B.Sc. (Hons) degree in Chemistry. Unife laid a very brilliant foundation for my postgraduate studies at University of Ibadan and to the glory of God; I breezed through graduate school in three and a half years with M.Sc. (1986; 71.4% average) and Ph.D. (1989) degrees in inorganic chemistry. My doctoral work on coordination chemistry titled 'Spectroscopic and Magnetic Properties of Oxovanadium (IV) complexes of aryl-, alkyl- and cyclo-monocarboxylates' with a heavy dose of theoretical calculations laid the foundation for my career in chemistry. Research in coordination chemistry is always a very thrilling experience; with preparation of transition metal complexes in the laboratory giving variety of beautiful colours. The colours of the complexes may give an inkling of what the geometry of the compounds could be before analysing your spectral and magneto- chemical data. With a very strong background in physical chemistry at Unife, I could not resist the nudge within me to complement my research with theoretical calculations using Normalized Spherical Harmonics (NSH) Hamiltonian to deduce geometries from spectroscopic data<sup>1-5</sup>.

### Video Clips

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### Scientific Origin and Evolution of Universe

The beginning of civilization confronted man with survival instincts on how to live successfully on planet earth and ever since he has started experimenting with various tools and materials. While I do not want to insult the sensibilities of religionists, my topic today on metals, which form an important group of elements in the periodic table makes it mandatory to talk briefly about its scientific origin and in doing so; also on what science teaches about the origin of the universe which is intricately involved with the formation of elements.

The most widely accepted theory for the origin and evolution of the universe to its present form is the 'hot big bang'. This supposes that all matter in the universe are contained in a

primeval nucleus of immense density ( $\sim 10^{96} \text{ g cm}^{-3}$ ) and temperature, ( $10^{32} \text{ K}$ ) which for some reasons exploded and distributed radiation and matter uniformly throughout space. The expansion of the universe resulted in cooling which allowed the four main types of force to be progressively differentiated thus permitting the occurrence of various types of particles. These forces are those of gravity, electromagnetism, and the weak and strong nuclear forces. One second after the 'big bang', after a period of extensive particle-antiparticle annihilation to form electromagnetic photons, the universe was populated by particles which sound familiar to Chemists- protons, neutrons and electrons. Shortly after, the strong nuclear force ensured that large numbers of protons and neutrons rapidly combined to form deuterium nuclei ( $p+n$ ) then helium ( $2p+2n$ ). The process of element building has begun. During this small niche of cosmic history, from about 10-500s after the big bang, the entire universe is thought to have behaved as a colossal homogeneous fusion reactor converting hydrogen to helium<sup>6-9</sup>.

Two other features of the universe are easily interpreted in terms of the big bang theory. The observation that the light received on earth from distant galaxies is shifted increasingly towards the red end of the spectrum as the distance of the source increase. This implies that the universe is continually expanding and, on certain assumptions, extrapolation backwards in time indicates that the big bang occurred some 15 billion years ago. The estimates provided from several other independent lines of evidence gives reassuringly similar values for the age of the universe. Secondly, the theory convincingly explains (indeed predicted) the existence of an all pervading isotropic cosmic black body radiation. This radiation which corresponds to a temperature of  $2.735 \pm 0.06 \text{ K}$  is seen as dying remnants of the big bang<sup>9</sup>.

### **Electronic Structure, Chemical Periodicity and the Periodic Table**

The concept of chemical periodicity is central to the study of inorganic chemistry. There is no known generalization that rivals the periodic table of elements in its ability to rationalize known chemical facts, predict new ones and suggest area for further study. Theodore Gray<sup>10</sup> described the Periodic Table as one of our civilizations iconic images instantly recognizable as the Nike logo, Taj Mahal or Albert Einstein hair. I cannot agree more. Nowadays, chemical periodicity and the periodic table find their natural interpretation in the detailed electronic structure of atom. The present views on the electronic structure of atoms are based on a variety of experimental results and theoretical models which are fully discussed in elementary texts. In a précis, an atom comprises a central, massive, positively charged nucleus surrounded by envelopes of negative electrons. The nucleus is composed of neutrons ( ${}^1_0n$ ) and protons ( ${}^1_1p$ ) i.e. ( ${}^1_1H^+$ ) of approximately equal mass tightly bound by the force field of mesons. The number of protons ( $Z$ ) is called the atomic number and this, together with the number of neutrons ( $N$ ), gives the atomic mass number of the nuclide

( $A=N+Z$ ). The charge on the electron ( $e^-$ ) is equal in size but opposite in sign to that of the proton and the ratio of their mass is  $\sim 1/1836$ .

## THE PERIODIC TABLE OF THE ELEMENTS

1 <u>H</u>																	2 <u>He</u>	
3 <u>Li</u>	4 <u>Be</u>											5 <u>B</u>	6 <u>C</u>	7 <u>N</u>	8 <u>O</u>	9 <u>F</u>	10 <u>Ne</u>	
11 <u>Na</u>	12 <u>Mg</u>											13 <u>Al</u>	14 <u>Si</u>	15 <u>P</u>	16 <u>S</u>	17 <u>Cl</u>	18 <u>Ar</u>	
19 <u>K</u>	20 <u>Ca</u>	21 <u>Sc</u>	22 <u>Ti</u>	23 <u>V</u>	24 <u>Cr</u>	25 <u>Mn</u>	26 <u>Fe</u>	27 <u>Co</u>	28 <u>Ni</u>	29 <u>Cu</u>	30 <u>Zn</u>	31 <u>Ga</u>	32 <u>Ge</u>	33 <u>As</u>	34 <u>Se</u>	35 <u>Br</u>	36 <u>Kr</u>	
37 <u>Rb</u>	38 <u>Sr</u>	39 <u>Y</u>	40 <u>Zr</u>	41 <u>Nb</u>	42 <u>Mo</u>	43 <u>Tc</u>	44 <u>Ru</u>	45 <u>Rh</u>	46 <u>Pd</u>	47 <u>Ag</u>	48 <u>Cd</u>	49 <u>In</u>	50 <u>Sn</u>	51 <u>Sb</u>	52 <u>Te</u>	53 <u>I</u>	54 <u>Xe</u>	
55 <u>Cs</u>	56 <u>Ba</u>	57* <u>La</u>	72 <u>Hf</u>	73 <u>Ta</u>	74 <u>W</u>	75 <u>Re</u>	76 <u>Os</u>	77 <u>Ir</u>	78 <u>Pt</u>	79 <u>Au</u>	80 <u>Hg</u>	81 <u>Tl</u>	82 <u>Pb</u>	83 <u>Bi</u>	84 <u>Po</u>	85 <u>At</u>	86 <u>Rn</u>	
87 <u>Fr</u>	88 <u>Ra</u>	89**										104						114 <u>Uuq</u>
			105 <u>Rf</u>	106 <u>Db</u>	107 <u>Sg</u>	108 <u>Bh</u>	109 <u>Hs</u>	110 <u>Mt</u>	111 <u>Ds</u>	112 <u>Uuu</u>	112 <u>Uub</u>							

* Lanthanide series	58 <u>Ce</u>	59 <u>Pr</u>	60 <u>Nd</u>	61 <u>Pm</u>	62 <u>Sm</u>	63 <u>Eu</u>	64 <u>Gd</u>	65 <u>Tb</u>	66 <u>Dy</u>	67 <u>Ho</u>	68 <u>Er</u>	69 <u>Tm</u>	70 <u>Yb</u>	71 <u>Lu</u>
** Actinide series	90 <u>Th</u>	91 <u>Pa</u>	92 <u>U</u>	93 <u>Np</u>	94 <u>Pu</u>	95 <u>Am</u>	96 <u>Cm</u>	97 <u>Bk</u>	98 <u>Cf</u>	99 <u>Es</u>	100 <u>Fm</u>	101 <u>Md</u>	102 <u>No</u>	103 <u>Lr</u>

**NOTE:** Yellow indicates alkali and alkaline earth metals; tan, transition metals; blue, main-group elements; gray, noble gases; and orange, lanthanide and actinide series  
© American Chemical Society

In addition to the prediction of new elements and their probable properties, the periodic table has proved invaluable in suggesting rewarding focus of research in the design and synthesis of new compounds. This becomes evident when an element or a group is altered in a compound and results in new effects and properties to that which is anticipated. It is the ability to anticipate the effect of changing an element or a group in a compound which enables effective construction of volatile precursors. I should also add that a prudent Chemist is always alert to the possibility of new effects or unsuspected outcome in every reaction which might surprisingly intervene. This mode of thinking has become totally entrenched in most Chemists that they seldom think of how extremely complex their work might be without the existence of periodic trends.



Mr. Vice-Chancellor, most of my research in the last three decades encompasses the design, synthesis and studying the properties of various compounds using the elements in the periodic table for beneficial applications to mankind. The design and construction of these mostly metal organic compounds, either for experimental purposes or theoretical studies involves the search for particular properties of choice and tuning the properties as necessary for target applications. In this molecular design, various elements of choice from the periodic table are reacted with often constructed electron donating groups of compounds (ligands) to form metal organic complexes which are routine in nature but are very important for intended applications. I will in the course of this lecture discuss some of these initiatives where my research group have contributed significantly to knowledge.

### **Transition Metal Catalysis and Butadiene Polymerization**

My decision to transfer my services to a University of Technology from University of Ibadan in September 1991, confronted me with a personal challenge to refocus my then largely academic and theoretical research for an applied edge. Luck came my way when in the winter of 1992; Montecatini s.p.a. and E.n.i. s.p.a two Italian conglomerates offered me a specialist training fellowship for six months at the International School of Advanced Studies in Polymer Sciences, University of Ferrara. I also had the privilege of a three months industrial training at Research and Development Laboratory of Enichem Elastomers, Grangemouth, Scotland, United Kingdom. This opportunity marked the beginning of my venture into materials science.

Generally, polymeric butadiene derivatives are of importance not only for basic research but also for their significant physical properties inclusive of elasticity, toughness, durability in various environments and wide temperature ranges over which the properties are retained. The most important single application has been, and remains, automobile tires which consume nearly  $3.0 \times 10^6$  metric tonnes per year in North America. The impetus for much of the research into other polydienes has been potential improvements in tires. Natural rubber, cis-1,4-polyisoprene has benefited from a psychological advantage since it is an old established commodity. However, being a natural commodity, it is exhaustible and there has always existed urgent need to find commercially more viable alternative 11-12.

Catalyst system based on neodymium has attracted tremendous attention for the polymerization of dialkenes. This is no doubt due to the fact that neodymium is the most active of the soluble rare earths and the system yields polymers with very high *cis*- content from several types of dialkenes e.g., butadiene, 2,3-dimethylbutadiene, 1,3-pentadiene and isoprene<sup>13</sup>. Recent trends in the production of elastomers have been towards products designed for specific use. This becomes imperative in the manufacture of high strength or molecular weight engineering materials<sup>14</sup>. The high molecular weight hydrocarbon

elastomer is very difficult to process because of the requirements of very powerful machinery capable of mixing and shaping very high viscosity polymers.

To overcome this problem, we have developed in our laboratories catalysts that will polymerize alkyldienes particularly 1,3-butadiene to a low molecular weight distribution and produce very low percent of high molecular weight materials with almost 100 % conversion of reactants to product<sup>15-17</sup>.

Table 1: G.P.C. Analysis of 1, 4-Polybutadiene obtained from NdV<sub>3</sub>/DIBAL-H/C.B.

Time (mins)	Conversion (%)	M <sub>n</sub>	M <sub>w</sub>	M <sub>v</sub>	MWD	% > 10 <sup>6</sup>
<b>(Catalyst age: 5 mins )</b>		(<--- x10 <sup>3</sup> --->)				
10	31	25	504	593	20.12	14.38
60	100	96	498	138	5.20	11.71
<b>(Catalyst age: 20 hrs)</b>						
10	26	81	862	589	10.6	23.92
120	100	75	621	67	8.3	17.09

Table 2: G.P.C. Analysis of 1, 4-Polybutadiene obtained from\*BD/NdV<sub>3</sub>/DIBAL-H/C.B.

Time (mins)	Conversion (%)	M <sub>n</sub>	M <sub>w</sub>	M <sub>v</sub>	MWD	% > 10 <sup>6</sup>
<b>(Catalyst age: 5 mins )</b>		(<--- x10 <sup>3</sup> --->)				
10	39	17	32	8602	1.9	0.04
120	96	81	225	355608	2.8	2.11
<b>(Catalyst age: 20 hrs)</b>						
10	26	30	55	8691	1.86	0.11
120	100	62	142	36147	2.28	0.26

NB: NDV<sub>3</sub>= Neodymium Versatate, DIBAL-H = Diisobutylaluminium hydride, C.B.= Crotyl bromide, \* BD = Butadiene.

Tables 1 and 2 display extracts of the result of the gel permeation chromatographic (GPC) analyses of the 1,4-polybutadienes obtained from the presented catalyst systems. The freshly prepared catalyst system NdV<sub>3</sub>/DIBAL-H/C.B (Table 1) gave a 100 % conversion of polymer one hour after preparation whereas the aged catalyst (20 hours) could only give the same conversion after 2 hours. This implies decrease in activity with ageing. For the butadiene modified catalyst (Table 2), both the freshly prepared and aged catalysts gave a 96 % product at full conversion time of 120 minutes. However, the monomer was found to have a stabilising effect on the catalyst system.

The macrostructure of the unmodified catalyst demonstrate a very broad molecular weight distribution with the aged catalysts displaying a higher percentage of high molecular weight materials while the modified catalyst has a very low percent of high molecular weight materials. In production processes where very low molecular weight product of rubbers are required, this product (Table 2) will be of great potential.

The microstructural properties of polymers obtained from both catalyst systems (Table 3) indicate that the unmodified catalysts display a higher percentage (98%) of cis-configuration.

Table 3: Microstructure of 1,4-Polybutadiene obtained on the Catalyst System

Catalyst	Age	Cis	Trans	Vinyl
		< ----- % ----- >		
Versatate	5 minutes	98.0	1.2	0.8
	20 hours	98.0	0.7	1.3
With 1,3-Butadiene	5 minutes	95.4	4.2	0.5
	20 hours	91.0	8.5	0.5

## PRECURSORS FOR THE CHEMICAL VAPOUR DEPOSITIONS OF CONDUCTORS AND SEMICONDUCTORS FOR ELECTRONIC APPLICATIONS

In the spring of 1997, the United States Office of Naval Research granted me a two year postdoctoral fellowship tenable at the Molecular Design Institute (MDI), School of Chemistry and Biochemistry, School of Materials Science and Engineering of Georgia Institute of Technology (Georgia Tech), Atlanta Ga. Research facilities at MDI are arguably second to none elsewhere even in the United States of America. All facilities required for laboratory research and instrumental analyses such as analytical, microscopy, spectroscopy,

crystallography and materials testing are all *en suite* in the School of Chemistry buildings and are available 24 hours daily all year round. The only impossible thing to do at MDI was only mind limited. It was undeniably, a dream come true to contribute to materials chemistry research of electronic devices. The industries represented by these advanced technologies have become a major contributor to the world economy and are responsible for improvement in the quality of lives we enjoy today. What may not be easily acknowledged is that most of the products derivable from these are not simply the product of research in physics and electrical engineering as commonly perceived; but are built on composite and rigorous research in chemistry and chemical engineering. The demand for smaller, faster and more complex electronic devices has been the driving force behind a broad spectrum of materials research.

Chemical Vapour Deposition (CVD) is defined as the preparation of a solid coating from a gaseous precursor by means of chemical transformation. The use of chemical vapour distinguishes CVD from physical deposition methods such as sputtering and evaporation, thus imparting versatility to the deposition technique<sup>18-19</sup>. CVD has become the method of choice in the growth of thin films over a large substrate area. The benefits of the method include non-line of sight, high throughput, low cost per unit, and uniform thickness and elemental composition coverage. CVD is practised in various formats; the processes differing in the means by which the chemical reactions are initiated. Some of these include Metal Organic Vapour Phase Epitaxy (MOVPE), Plasma Enhanced Chemical Vapour Deposition (PECVD), Photo CVD, Low Pressure Chemical Vapour Deposition (LPCVD), Combustion Chemical Vapour Deposition (CCVD), Aerosol Assisted Chemical Vapour Deposition (AACVD)<sup>20-23</sup>. Each of the methods have their advantages and disadvantages, their use is dependent on the size and complexity of the device being prepared.

#### SCHEMATIC DIAGRAM OF A CVD

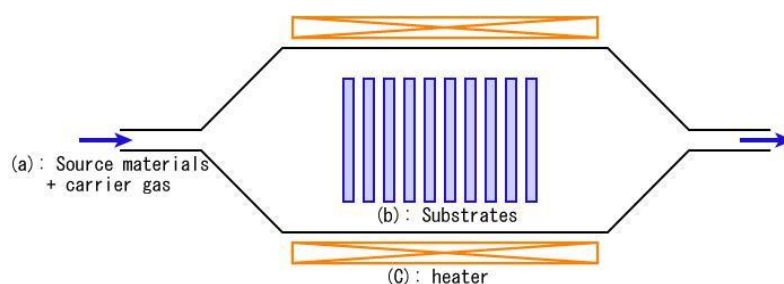


Fig 1: Hot-Wall Thermal CVD (Batch Operation Type)

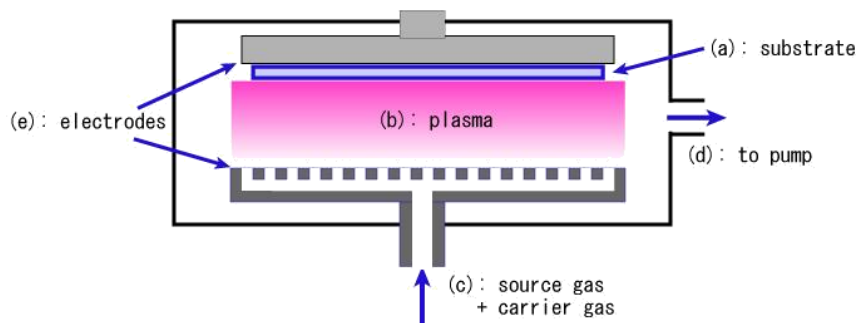


Fig 2: Plasma Assisted Chemical Vapour Deposition (PACVD)

### Properties of Precursors for CVD

The precursor which is one of the most important components of the CVD systems often referred to as the source, must be thermally stable in the solid as well as the vapour phase up to delivery temperature<sup>24</sup>. The first step in the CVD process is vaporization of the precursor at a pressure of at least 100 mTorr. Liquid precursors at ambient temperatures are preferable to solids in achieving reasonable deposition rates. This prevents premature decomposition from occurring at the source, or in the lines leading to the substrate. In order to give a film with the desired composition, morphology and purity the precursor must undergo controlled thermal decomposition at substrate temperature. It is therefore necessary to find a precursor that is thermally stable at source temperature but decomposable at substrate temperature<sup>19</sup>.

Precursors usually take the form of organometallic or metal-organic compound with the metal being a major component of the desired film. The properties of the material being grown are highly dependent upon the purity, as well as the chemical make-up and decomposition pathway of the precursor<sup>24</sup>. This is where the design and construction of suitable ligand system becomes inevitable. This no doubt requires sagacity at building and designing molecules that will fit the desirable properties as defined.

### GROUP II METAL ALKOXIDES

Mr. Vice Chancellor, our interest in precursor chemistry has been mainly in the alkoxide chemistry of group 2 metals which is very rich and diverse. Simple binary and ternary oxides of high purity are of considerable importance in the development of materials. Thin oxide layers are in great demand for electronic materials and efforts to synthesize volatile metal alkoxides precursors have increased<sup>25</sup>. A significant amount of research conducted in this area has been directed toward the reduction of intermolecular interactions, and the preparation of volatile monomeric compounds. Group 2 metal alkoxides can easily be

prepared from the corresponding alcohol. The reaction, depending on the alcohol, can be carried out by combining the group 2 metal with the appropriate alcohol. In some cases the reaction can be carried out in the presence of liquid ammonia or ethanol. This method makes use of the intermediate metal-amide or metal-alkoxide, and proceeds via ligand exchange<sup>26-28</sup>. The heavy group 2 compounds of simple monoanionic alkoxides, like methoxide and ethoxide, exist as polymers in the solid state since each ligand is monodentate<sup>29-30</sup>. The first compound of calcium alkoxide soluble in non donor solvent is  $\text{Ca}_9(\text{OCH}_2\text{CH}_2\text{OMe})_{18}(\text{HOCH}_2\text{CH}_2\text{OMe})_2$  (Fig 3).

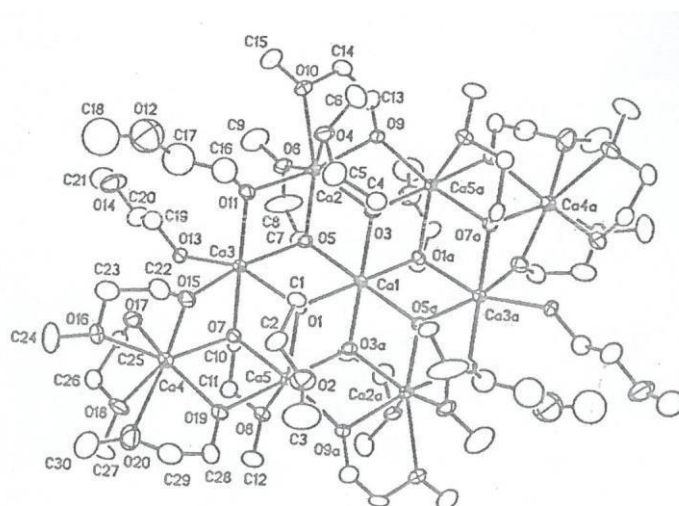


Fig 3: Ortep structure of  $\text{Ca}_9(\text{OCH}_2\text{CH}_2\text{OMe})_{18}(\text{HOCH}_2\text{CH}_2\text{OMe})_2$

Other workers investigated an extension of this motif in an attempt to further reduce the molecularity of group 2 alkoxides. Rees and Moreno<sup>31</sup> proposed the first example of a monomeric barium *bis*-alkoxides. The proposed solution structure determined by cryoscopic and spectroscopic data is shown in Fig 4. This ambient temperature liquid exists as monomer in the solution state, although oligomeric species prevail in the absence of solvent.

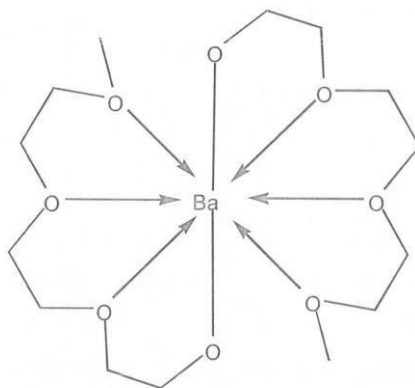


Fig.4: The proposed solution structure as determined by cryoscopic measurement

The theme of coordinatively saturating the metal center of heavy group 2 elements has yielded several molecular compounds; however, their volatility and vapour phase stability are insufficient for CVD applications. Sterically demanding aryloxides investigated by some researchers with some group 2 metals also yielded oligomers often with presence of solvent molecules making them also unsuitable for CVD applications<sup>29-30</sup>. The simplest of the compound was prepared by reacting strontium metal with phenol in THF at reflux. Crystallization of the product resulted in a tetramer<sup>32</sup> with two different strontium environments, six molecules of THF and two neutral ligands  $\text{Sr}_4(\text{OPh})(\text{PhOH})_2(\text{THF})_6$ . Homoleptic monomeric alkoxides are very rare.

### Our Contributions

In our laboratory, we have used trimethoxyphenyl alcohol in combination with intramolecular Lewis base stabilization motif to obtain the first series of homoleptic, monomeric heavy group 2 metal alkoxide which have been structurally characterized using single crystal X-ray diffraction technique. Our approach was to avoid coordinating solvents and use dried non-coordinating solvents during the synthesis of the metal complexes.

### Synthesis of the ligands:

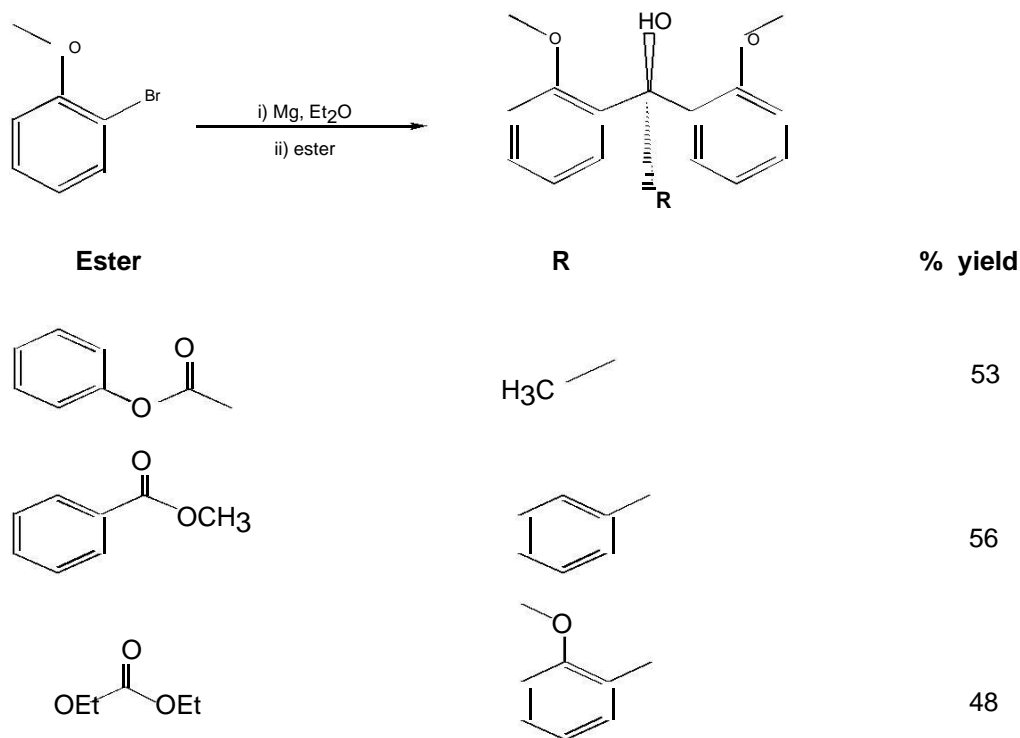
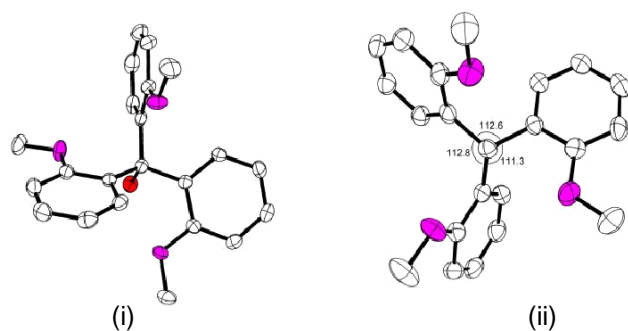
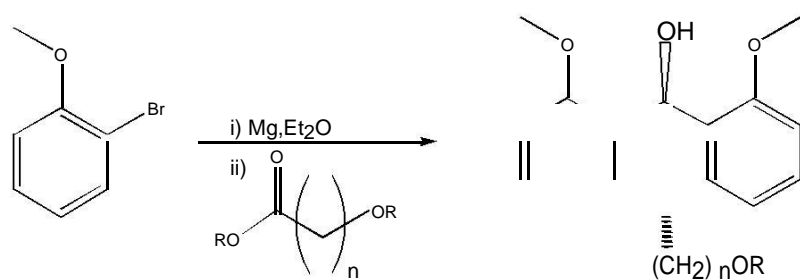


Fig 5: Preparation of bis(anisole)methanol[BAM] Derivatives



- (i) *tris*(2-methoxyphenyl)methanol (R = 3.74%)  
(ii) *tris*(2-methoxyphenyl)methane (R = 6.51%)

Fig 6: Ortep representation of some of the X-ray Structures of the Ligands



<u>Ester</u>	<u>R</u>	<u>n</u>	<u>% yield</u>
methyl-3-methoxypropanoate	Me	2	58
methyl-4-methoxybutanoate	Me	3	61
ethyl-4-ethoxybutanoate	Et	3	52
methyl-5-methoxypentanoate	Me	3	69

Fig 7: Preparation of Ether-containing bis(anisole) [EC-BAM] Derivatives



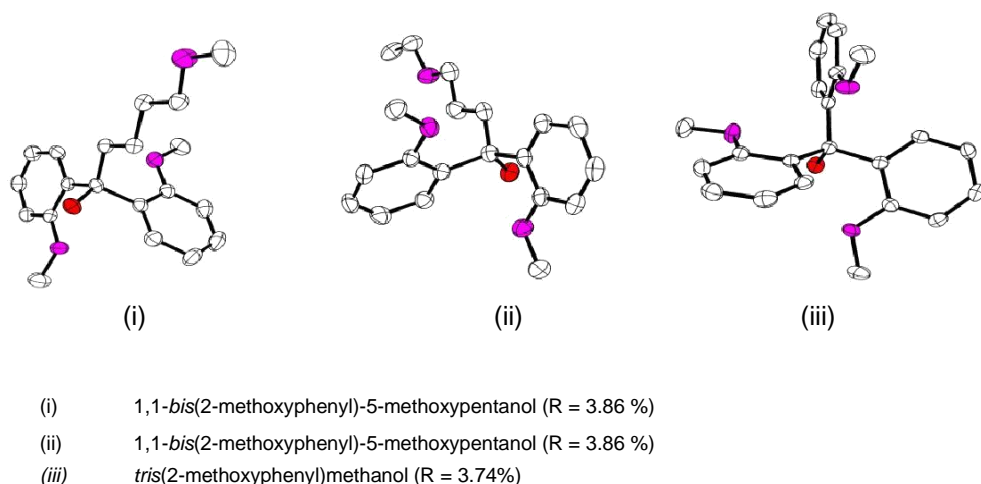
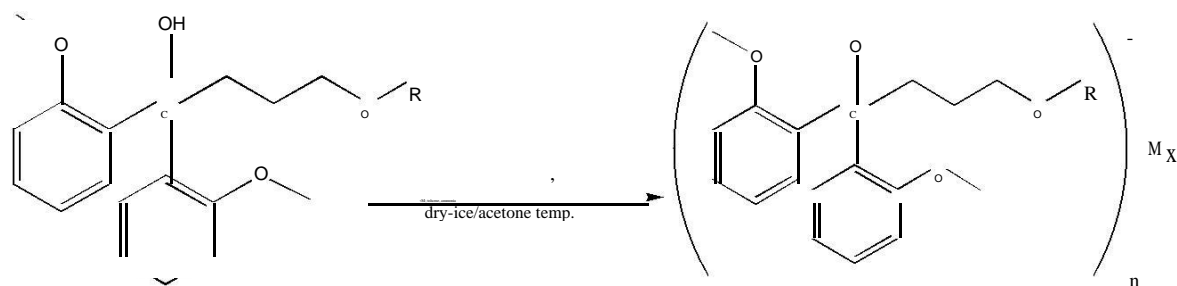


Fig 8: Ortep Representation of X-ray Crystal Structure of some of the EC-BAM Ligands

### Experimental design of the Barium alkoxides

The ligands used for the preparation of barium alkoxides and other group 2 metals were tailor-made for the metals to combine the advantages of steric overcrowding and coordinative saturation within same species. The metal complexes were prepared by ammonia catalyzed reaction of the metal granules in aromatic hydrocarbon solvent.



(1) R = Me, M = Ba, n = 4, x = 2; (2) R = Et, M = Ba, n = 4, x = 2; (3) R = Et, M = Ca, n = 8, x = 4

Fig. 9: Schematic diagram for preparation of Barium Alkoxides

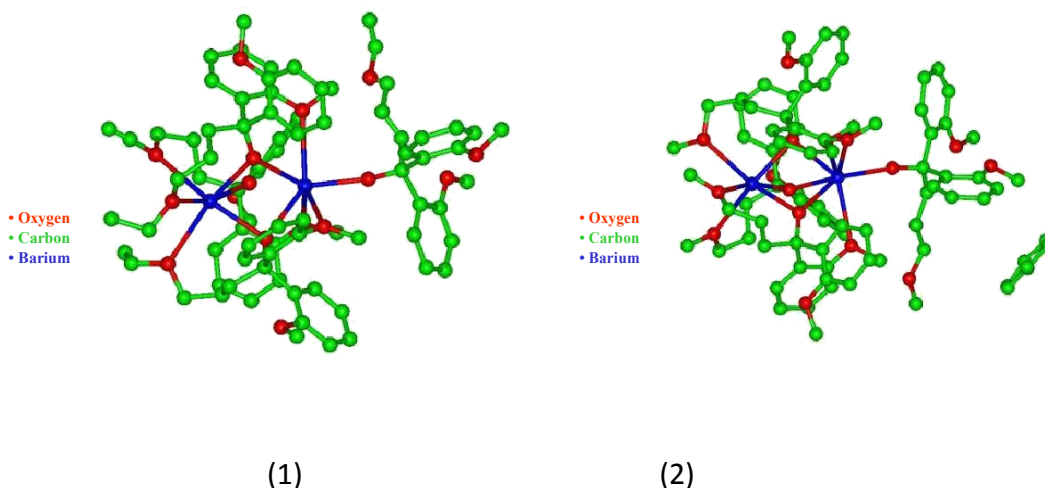


Fig 10: Ball and stick representation of the structures of Ba<sub>2</sub>[OC{o-C<sub>6</sub>H<sub>4</sub>OMe)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OEt}<sub>4</sub>] (1) and Ba<sub>2</sub>[OC{o-C<sub>6</sub>H<sub>4</sub>OMe)<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>OEt}<sub>4</sub>]C<sub>7</sub>H<sub>8</sub> (2)

X-ray diffraction studies of the barium compounds show that the compounds adopt a dimeric structure with three bridging and one terminal alkoxide ligand giving the two metals distinct environments. The barium complexes displayed stunning geometries with the barium metals in structure (1) exhibiting six-coordinate distorted octahedron while those in structure (2) adopt both six and seven coordinate geometry. The dimeric nature of the barium alkoxides is a marked improvement over the oligomeric alkoxide analogs which were known previously in the literature. Variable temperature solution N.M.R. studies (<sup>1</sup>H and <sup>13</sup>C) suggests that there is a dynamic equilibrium between several environments resulting in single observed resonances for most <sup>1</sup>H and <sup>13</sup>C environments within the compounds<sup>33</sup>.

The isolated calcium alkoxides in the series is tetrameric with two of the calcium ions displaying a five coordinate geometry while the remaining pair adopts a six coordinate geometry; and all the four metal atoms arranged in a hexagonal core (Fig 11). This is a very marked improvement on the Ca<sub>9</sub> nonahedral metal core reported earlier (Fig 3).

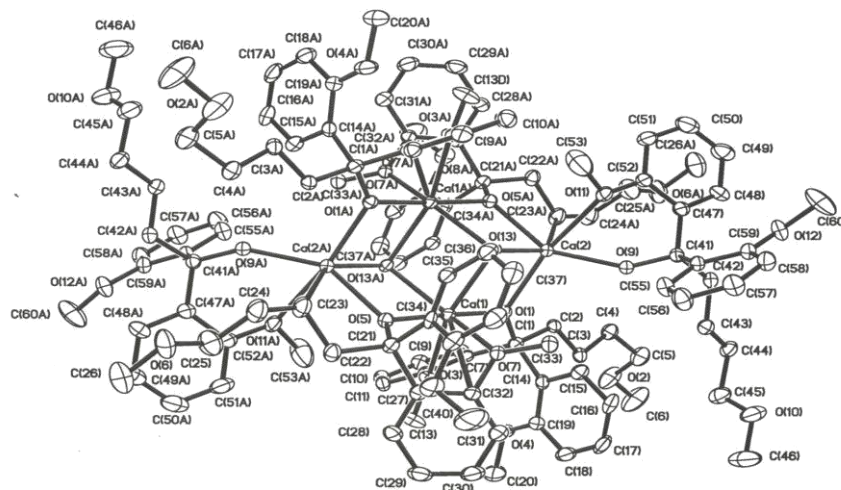


Fig 11: Ortep Representation of X-ray Crystal Structure of  $\text{Ca}_4[\text{OC}\{\text{o-C}_6\text{H}_4\text{OMe}\}_2(\text{CH}_2)_4\text{OMe}]_4$

Among the late group (I) elements; potassium (K), rubidium (Rb) and caesium (Cs) have been known to play important roles as components of “superbases”. The structural examinations of these species are rare in comparison with their lighter congeners in the same group (Li and Na). With our success in employing intramolecular coordination to great benefit in the chemistry of Group II alkoxides, we also explored behaviour of caesium with these ligands to afford very finicky structures. The four caesium metal atoms (Fig. 12) in dynamic equilibrium formed a cuboid surrounded by the coordinate ligands. Overall, the study produced more than 30 precursors with twenty of them characterized by single crystal X-ray diffraction exclusive of the alkali metal alkoxides. A couple of them also were found to be useful as precursors in some types of CVD applications.

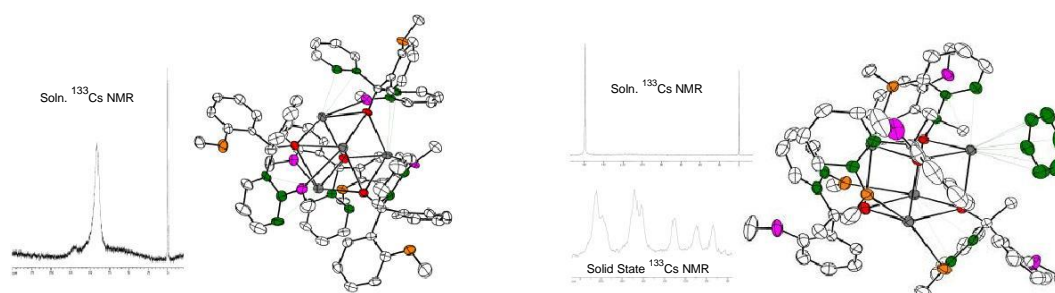


Fig. 12: Ortep representation of the X-ray Structure of some Caesium Alkoxides  $[\text{CsOR}]_4$

After returning home in April 1999 and spending the remaining part of the year observing different types of unions strike, I had no option but to accept a position as Professor of Chemistry at the University of the North, Sovenga, South Africa in January 2000 having been appointed to the position in December, 1998.

I should add that the research environment and facilities at Sovenga apart from restoring my sanity in continuing my laboratory research greatly assisted in sorting out major part of some of my doctoral students instrumental research work. It also afforded focus and opportunity to tidy up work that had been pending from our previous research on coordination chemistry especially transition metal complexes of  $\beta$ -ketoamines and adducts with nitrogenous bases<sup>34-40</sup>, substituted benzoic acid hydrazides<sup>41-44</sup>,  $\beta$ -diketonates<sup>45-47</sup> and their mixed ligands with hydrazides<sup>48</sup>.

## **THEORETICAL STUDIES ON NANOTECHNOLOGY AND MATERIALS**

Nanotechnology is the development and utilization of structures and devices with molecular size range 1-20 nm. During the past two decades, 'small particle research' has become quite popular in various fields of chemistry and physics. These are particulate semi-conducting materials most often referred to as quantum dots, Q particles or nanoparticles. Current interest in this emerging technology<sup>49-50</sup> of the 21<sup>st</sup> century is broad based and includes but not limited to the following:

- ❖ Synthesis, processing, properties, characterization, modeling, simulation and use of nanostructured materials including high rate production of nanoparticles for potential industrial use.
- ❖ Research on nanoscale materials for energy applications with focus on synthesis and processing of materials with controlled structures, surface passivation and interface properties with target applications in catalysis, opto-electronics and soft magnets.
- ❖ Biomimetics, smart structures, micro devices for tele-medicine, compact power sources, superlattices and buckminsterfullerene are developed in interdisciplinary environments.
- ❖ Nanoparticles are used in drug delivery, in particular drugs that have poor solubility are coated with polymers to provide controlled release systems.
- ❖ Nanoparticulate silver is commercially produced in antibacterial dressings while nanoparticulate zinc has been used as a fungicide.

## Theoretical Background

Quantum chemistry started when Heitler and London treated the covalent bonding in the hydrogen molecule. An early goal that emerged immediately after World War II was what is known as *ab initio* calculations, where chemical conclusions were obtained from the general principles of quantum mechanics. Traditionally, quantum chemistry is based on the non-relativistic Schrodinger equation and the Born-Oppenheimer (clamped-nuclei) approximation. Thus, a level of approximation, such as Hartree-Fock, and technical details such as a basis set, had to be chosen first, with each choice yielding what later came to be known as 'model chemistry',<sup>51</sup>.

Beyond teaching us a great deal about how molecules behave and interact with their environment, quantum chemistry has yielded a very important product: software packages, some of them representing commercial enterprise and others given away freely to help others further the cause of science. In either case, these programs are being used by an ever-growing base of users. It has been opined, and rightly so that 'the very many capabilities of some of the better packages are such that their use by inexperienced is a bit like putting a learner driver behind the wheel of a Ferrari or Bugatti'. It is undeniable that many branches of chemistry utilize the efforts of the quantum chemists through the software that they have produced<sup>51</sup>.

Computational Chemistry, molecular modelling and dynamic simulations of fundamental chemical processes can be carried out at atomic and molecular level using relevant software on laptops or high performance computing (HPC) cluster machine. These quantum chemical studies allow existing materials to be refined and its properties studied and new materials designed often with unique properties. It employs calculations side by side with wet chemistry to provide insight that may sometimes be unobtainable experimentally. Some of the practical aspects of computational chemistry include but not limited to:

- ❖ Simulation/modelling of structural features of molecules, visualizing electronic structures and electronic potentials, conformational searching, visualizing molecular orbitals.
- ❖ Analysing reaction thermodynamics, building and characterizing reactive intermediates, transition state modelling, and thermodynamic vs kinetic control in reactions.
- ❖ Predicting spectroscopic data (IR, NMR, UV/Vis etc) including solvation effects,
- ❖ Simulation of drugs-enzymes interactions, Quantitative Structure Activity Relationship (QSAR) and Quantitative Structure Property Relationship (QSPR) of medicinal compounds/molecules
- ❖ Reactive intermediates in reactions, isotope effects, thermodynamic vs kinetic control in reactions, conformation, frontier molecular orbital theory and reactivity

This approach provides alternative cost-effective and environmentally friendly approach to synthetic chemistry before embarking on laboratory work. It is also of great benefit prior to engineering scale up and design of industry process.

### **Our Contributions**

Mr. Vice-Chancellor, our interest in nanotechnology is on electronic materials such as transistors, solar cells which we have examined for superior qualities in terms of structure, optical and magnetic properties. The unfavourable research environment, acute challenges in accessing relevant research facilities and dearth of funding revived my interest in computational chemistry.

Our research in computational chemistry is based on the application of quantum chemical methods to address chemical problems. The research focuses on design, synthesis and development of molecules specifically tailored and optimized for field effect transistors, electro-active, photovoltaic and electroluminescent applications<sup>52-56</sup>. The computational modeling affords the opportunity of calculating both macroscopic and microscopic properties of the studied compounds.

Apart from computational modeling, some of the compounds have been synthesized and characterized using electronic, nuclear magnetic resonance (NMR), infrared and Raman Spectroscopy as well as X-ray diffraction techniques. The synergy of combining theoretical studies with laboratory work thereby confirming our formulated methods brings out the splendour in advancing theoretical postulations. We have used quantum chemical calculations to give insight to the molecular properties and descriptors that are responsible for corrosion inhibition of some organic molecules used as inhibitors and adsorption of some dyes (such as Congo red and malachite green) from aqueous medium. These findings have contributed to the literature on adsorption and inhibitory mechanism of the dyes<sup>57-63</sup>.

We have also investigated [4+2] Diels-Alder reaction mechanisms using cyclopenta-2,4-dienethiones and cyclopenta-2,4-dienones with fullerene 60 for the synthesis of new molecular compounds of biological import. The structural properties of some coordination compounds with amorphous properties have been studied and their plausible structures and geometries predicted. The predicted structures and calculated spectroscopic data compare favorably well with contiguous complexes determined experimentally by single crystal X-ray diffraction and spectroscopic techniques<sup>65-68</sup>.

## Novel Synthesis of Coordination Compounds and their Applications

In our laboratory, we have prepared over the years thousands of coordination and organometallic compounds. Most of these compounds address structure activity relationships of biologically active compounds, luminescence, magnetic, non-linear optical properties, molecular recognition, catalysis, semi- conductors and Organic Light Emitting Diodes (OLED)<sup>69-80</sup>. Our recent work on ruthenium (II) and copper(II) mixed - ligand complexes with potential applications in various electrochemical and photophysical processes including probes of DNA structures is noteworthy<sup>81</sup>.

The importance of mixed-ligand complexes in biological processes, analytical chemistry, catalysis and magnetochemistry has been well documented. Complexes with  $\pi$ -acceptor ligands such as 2,2-bipyridyl (bipy) and 1,10-phenanthroline often form extremely stable ternary complexes both in solution and solid state. The increasing use of these two ligands in the interaction of DNA with protein where  $[(\text{phen})_2\text{Cu}]^+$ ,  $[(\text{phen})_2\text{Cu}]^{2+}$  and  $[(\text{phen})\text{Cu}]^+$  were discovered to be the active species for DNA cleavage has increased the resurgence of studies on these two ubiquitous ligands in various laboratories including ours<sup>82-85</sup>.

Some of our mixed ligand complexes particularly  $[\text{Cu}(\text{phen})_2\text{Cl}\cdot 6.5\text{H}_2\text{O}]$  {CCLP} and  $[\text{Cu}(\text{phen})_2](\text{phen})_2(\text{NO}_3)_2\cdot(\text{H}_2\text{O})_8$ {CENP} have been found to be very useful as self indicating agents for complexometric titrations. The two compounds have been successfully used to determine ascorbic acid contents of pure ascorbic acid and in different leafy vegetables and fruits. The comparison of the results with a well known standard 2,6-dichlorophenolindophenol (DCPIP) showed an improvement over the standard. In addition the two compounds have been found to be very stable in air, not deliquescent and fulfilled all requirements for titrimetric analysis and their patents are pending. The impact of the use of these compounds to replace DCPIP in foods and beverages industry as well as medical establishment will be intense<sup>86-90</sup>.

## Metal Organic Framework

Metal-Organic Frameworks, or MOFs, have emerged as an extensive class of crystalline materials with ultrahigh porosity (up to 90% free volume) and enormous internal areas, often, greater than  $600 \text{ m}^2/\text{g}$ . These properties together with extraordinary degree of variability for both the organic and inorganic components of their structures make MOFs of importance for potential applications in clean energy; most significantly as storage media for gases such as hydrogen and methane and as high capacity adsorbents to meet various separation needs<sup>91</sup>. Additional applications in membranes, thin film devices, catalysis and biomedical imaging are increasingly gaining importance.

One of the hallmarks of MOFs is their topologically diverse and aesthetically pleasing structures, many of which are derived from minerals in nature. Designing a target structure with specific properties and function represents an eternal aspiration for material scientists.

## Our Contributions

Our interest in MOFs is to construct compounds bearing various functional properties, with three functionalities: NLO activities, magnetism and gas storage. One of the basic features required for NLO active materials is an acentric structure, which can potentially be induced through the introduction into the structure of an asymmetric ligand. For the construction of porous MOFs, ligands with rigid units (such as phenyl and pyridyl groups) are preferable. Short and conjugated bridges within MOFs are efficient for magnetic coupling, and analogs of aromatic rings are typical conjugated groups. In order to achieve the goal of preparing multifunctional MOFs, a ligand containing rigid units and asymmetrically arranged O/N donors can be assembled with magnetic transition metal ions<sup>92-93</sup> such as Mn<sup>II</sup> and Cu<sup>II</sup>.

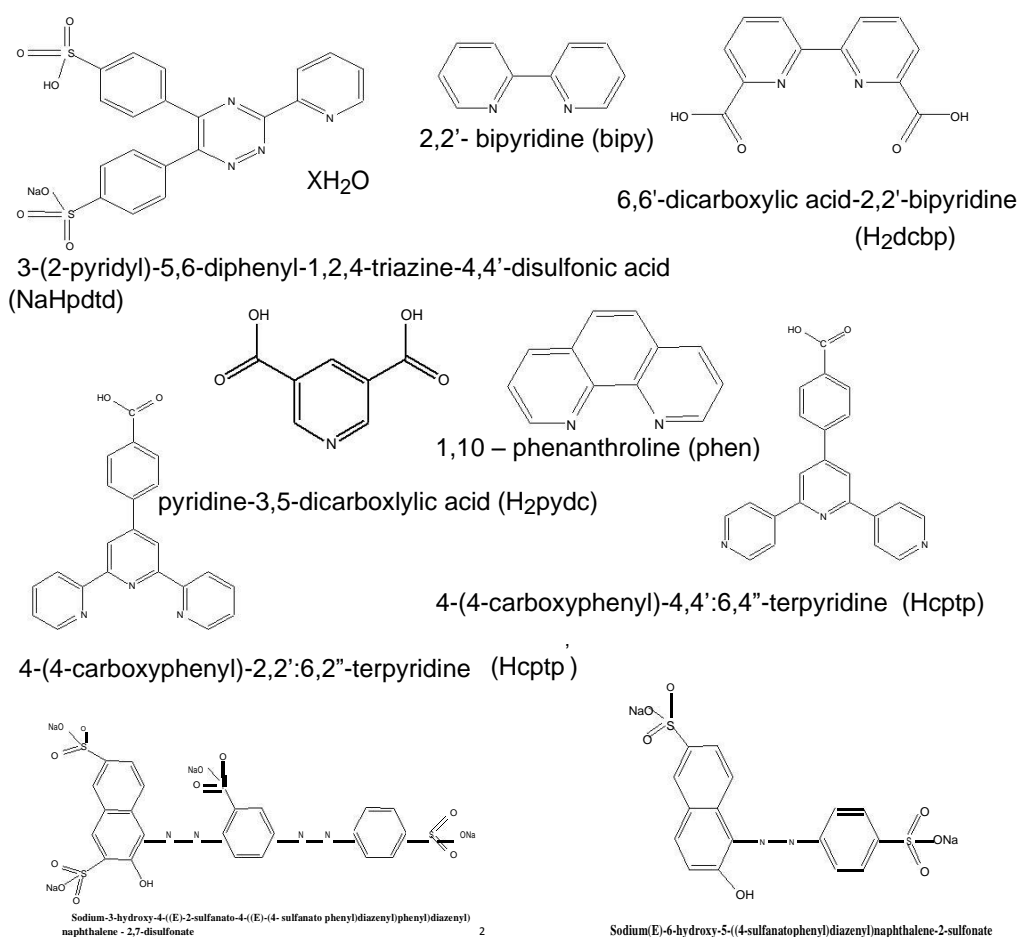
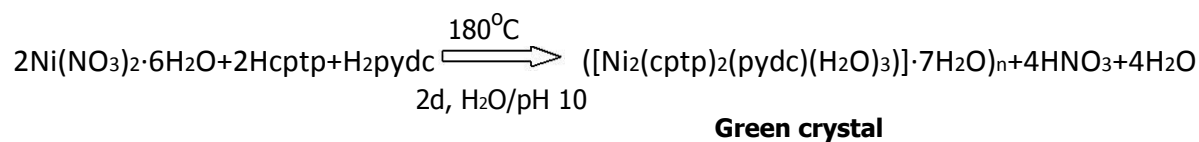
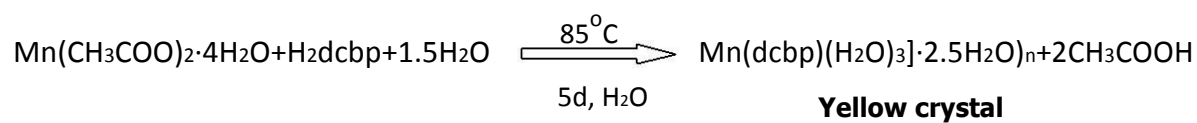
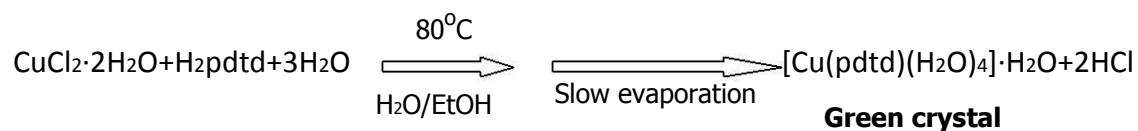
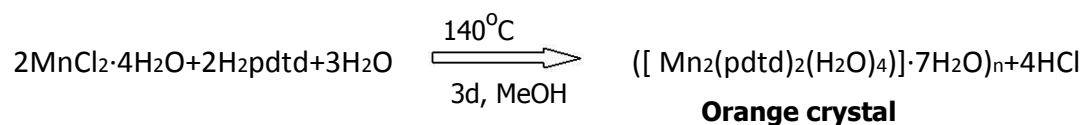


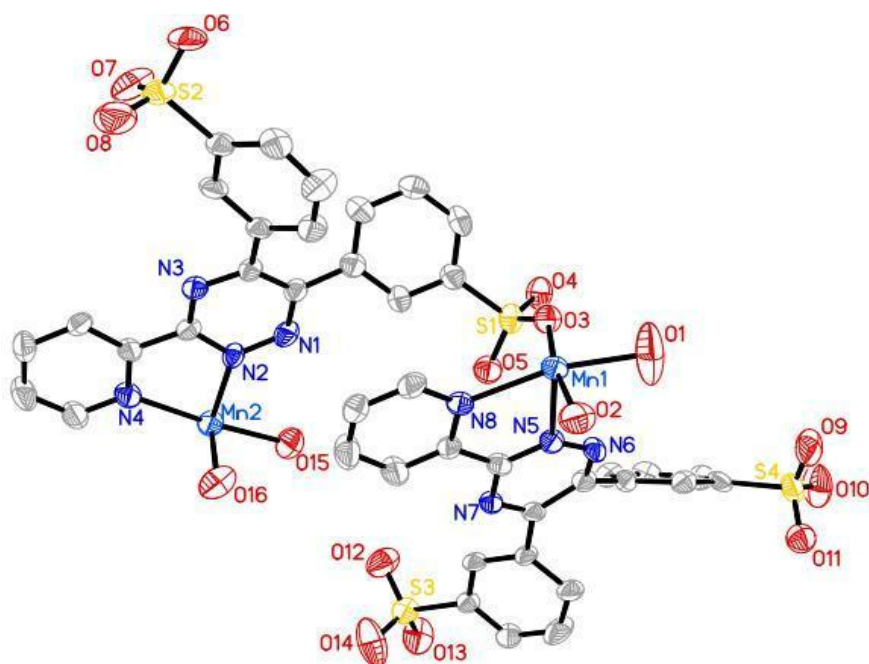
Fig 13: Some Representative Ligands of Interest



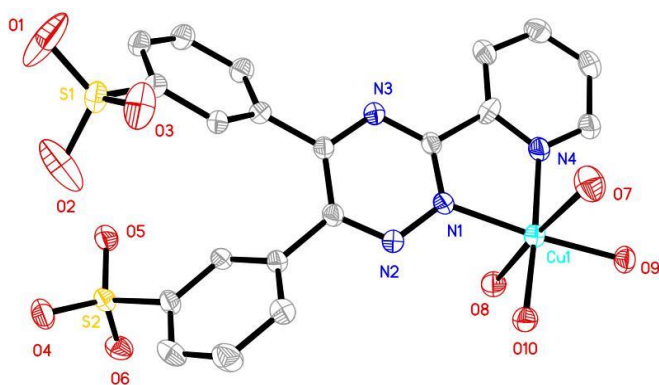
## Typical Synthetic routes for formation of the complexes



(a) Structure of  $([\text{Mn}_2(\text{pdt})_2(\text{H}_2\text{O})_4] \cdot 7\text{H}_2\text{O})_n$



**(b) Structure of [Ni(ptdt)(H<sub>2</sub>O)<sub>4</sub>]**



**(c) Structure of [Cu(ptdt)(H<sub>2</sub>O)<sub>4</sub>] · H<sub>2</sub>O**

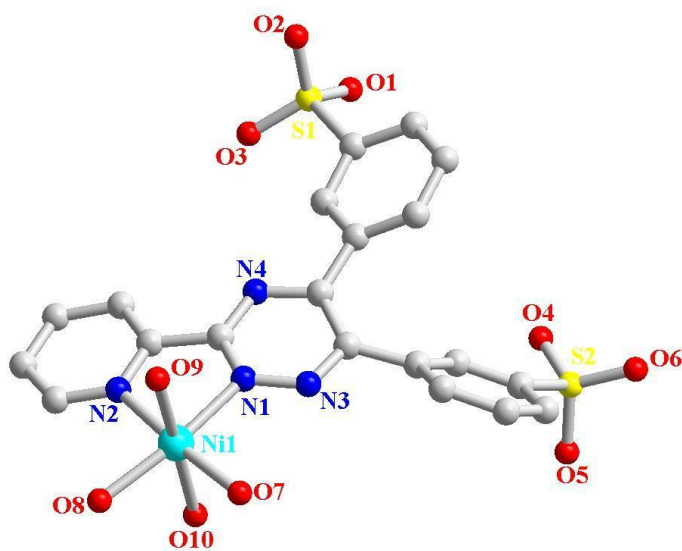


Fig. 14 (a-c): X-ray Single Crystal Structures of some Metal Organic Framework

## Conclusion

The importance of materials science in our present age cannot be overemphasised. Advanced technologies from microelectronics and nanostructures to spacecraft and biosensors depend absolutely on amazing materials created through the ingenuity of scientists and engineers. In the past few years, techniques have been developed to assemble molecule by molecule and atom by atom; we literally have the ability to move single atoms and place them where needed. The possibilities that power brings to the molecular architecture and processing of newer “smarter” materials are better imagined.

The opportunities are not only mind boggling, they are also mind limited; whatever we can think about now can easily be achieved. The socio-economic impact of materials in the developed countries is also staggering. In United States alone, it is estimated that the industries of aerospace, automobiles, biomaterials, chemicals, energy, metals and telecommunications-all critically dependent on materials-together generate about \$4.0 trillion in sales annually and employ about 10 million people. Nigeria can emulate this to solve its unemployment problems.

We have over the years been able to contribute to knowledge in various areas of sciences particularly in the design, construction and architecture of molecules for beneficial applications to meet human needs. We have developed soluble Ziegler-Natta Catalysts using neodymium catalysts for stereospecific polymerization of alkyldienes particularly butadienes for production of elastomers useful in automobile and aircraft tire production.

Our research on development of precursors useful in metal organic chemical vapour depositions (MOCVD) has produced among others the first homoleptic monomeric barium alkoxide by employing donor functionalized ligands that combines the advantage of steric overcrowding and coordinative saturation within same species. The studied ligand systems has equally produced a range of alkali metal alkoxides particularly caesium alkoxides with a range of interesting topological single crystal X-ray structure; a very rich addition to chemistry of group 1 metals.

Our studies on computational chemistry have been focused on design, synthesis and development of compounds optimised for field effect transistors, photovoltaic and electroluminescent applications. This is a cost-effective and environmentally prudent approach to synthetic chemistry before embarking on laboratory work. The thousands of coordination compounds prepared over the years in our laboratories have addressed structure activity relationships of biologically active compounds in addition to various applications in catalysis, semi-conductors, electrochemical and photophysical processes

including probes of DNA structures. Our research on metal organic frameworks (MOFs) are of great potential for applications in clean energy, storage media for gases, catalysis and biomedical imaging.

Mr. Vice - Chancellor, our bodies are made up of molecules with various biological and chemical reactions taking place every second. Over the last thirty years, we have used various metals and ligands -which are largely electron donating- to design and construct molecules which bear a similar corollary to design of buildings (in Architecture) for various uses which are beneficial to mankind in polymer industries, photonics, analytical, food and beverages, materials sciences, biological systems, as well as in fundamental research that drives various applications. This has been possible by the juggling of metals and electrons and tuning those properties of interest as desired for technological advancement.

## **RECOMMENDATIONS**

I want to plead that we should encourage our young lecturers to benefit from opportunities of research in advanced laboratories. It is sad that establishment issues are preventing some of our young and creative colleagues from travelling abroad for postdoctoral research. Mr. Vice-Chancellor sir, please look into this. The exposure I had in various laboratories has assisted in training as of today 8 doctoral students for LAUTECH in various specializations three of who are full Professors now and two Readers in Chemistry. No doubt this has impacted positively on the University and the quality of research coming out from this group of scholars. I also wish to make the following recommendations:

1. Our undergraduate curriculum in science and engineering should be reviewed to assist our students fit into the new realities and advances in science and technology worldwide. This becomes more important if we want to continue to produce competitive graduates.
2. Training of our postgraduate students should be improved to expose them to full complements of available facilities in their respective fields. While this may sometimes be difficult within the country; an institutional policy change backed by Government assistance would greatly assist in this endeavour.
3. Researchers should be encouraged to participate in multidisciplinary/ interdisciplinary research where individual contributions can be recognised, appreciated, prized and nurtured. The need to develop renewed partnerships is more now than ever, particularly so when the technology for doing certain kinds of science and engineering is so expensive.

4. Government should establish a National Research Foundation similar to what obtains in developed countries and some countries in Africa to promote, nurture and document research activities in various Universities and research Institutes for national development. This becomes inevitable now that all countries of the world are moving away from commodity based economy to knowledge economy.
5. Recognising the importance of materials science and engineering, researchers in complementary disciplines need to formulate needs initiative for our Nation which are myriads and present to government. We also have to leverage on our diverse academies and professional societies to educate the policy makers on this critical area of research and the benefits derivable.

## ACKNOWLEDGEMENTS

I have been richly blessed by God using different people at different times throughout my studentship days and working career particularly during the period I held administrative responsibilities in various Institutions both at home and abroad. I thank you all most sincerely from the bottom of my heart.

Specifically, I want to express my deepest gratitude to my parents, Ven. S.O. Odunola & Chief (Mrs) C.O. Odunola for their sacrifice, love, care and support over the years. They pushed me to the limits of my potentials challenging me to strive for nothing but the best; asking me at each milestone whether what I thought I had achieved was my very best. I also want to thank my siblings, Oluyinka, Olugbenga, Olutayo, Ibukun, their spouses, and our in-laws for their love, support and understanding over the years. My hearty appreciation to Mrs. T. A. Osowole, and our families, The Oluwoles, The Odunolas, The Sannis, The Akintundes and The Osowoles for their love and understanding.

I wish to thank all my teachers from primary school to University level for the tutelage under them which has moulded me to the person I am today. My very sincere appreciation to late Prof. K.S. Patel and Prof. G.A. Kolawole who taught me the rudiments of Inorganic Chemistry; and Dr. David Wilson and Dr. Peter Ansel; my colleagues at Research and Development Laboratory, Enichem Elastomers, Grangemouth, Scotland for their assistance and support during the biting winter of 1992/1993 in Scotland. I also wish to register my profound gratitude to Dr. Williams S. Rees Jr. and the group members at Molecular Design Institute, School of Chemistry and Biochemistry, School of Materials Science and Engineering, Georgia Institute of Technology the unfettered use of facilities in the laboratories.

I received generous research grants from many organizations without which my exposure, research and training in advanced laboratories wouldn't have been possible. I therefore wish to register my indebtedness to the following:

1. Third World Academy of Sciences (TWAS) & International Centre for Theoretical Physics (ICTP), Trieste, Italy for various research visits, training fellowships and research grants.
2. Montecatini spa/E.n.i. spa the Italian conglomerates for the scholarship to attend School of Advanced Studies in Polymer Sciences at the University of Ferrara, Italy
3. Georgia Institute of Technology, Atlanta Ga. USA, United States Office of Naval Research and Defence Advanced Research Project Agency (DARPA) of United States.
4. International Centre for Science and High Technology and International Centre for Pure and Applied Chemistry.

5. United Nations Industrial Development Organization.

6. University of the North, (now University of Limpopo), Sovenga, South-Africa.

My deepest gratitude to my cherished brothers from other parents and research associates Prof. Joseph Woods and Prof. Oladapo Bakare and their spouses for over three decades of fellowship, love and support. I also want to thank Prof. & (Mrs) O.A. Alabi, Prof. & (Mrs) I. A. Adeyemi, Prof. & (Mrs) O.O.P. Faboya, Engr. M.A. Owoade, Mr. & Mrs. Fola Owolabi, Mr. & Mrs. Yomi Akintunde, Mr. & Mrs. Toyin Akintunde, Mr. & Mrs. Fola Ajiboye and all my friends especially, Prof. & Dr. (Mrs) F.A. Adekola, Prof. J.A. Obaleye, Prof. Jason Mathews, Prof. Aifheli Gelebe, Engr. & Dr. (Mrs) Sina Arulogun, Engr. & Mrs Tunde Oyelakun, Hon. G.R. Kareem and Hon. Wumi Oladeji and many others too numerous to mention, may the good Lord reward you.

I wish to register my profound gratitude to the foundation Vice Chancellor of LAUTECH, Prof. Olusegun Ladimeji Oke, FAS and late Mrs Aduke Oke for their love, parental role and assistance in supporting my career. I also wish to acknowledge the supports received from former Vice Chancellors; late Prof. A.M. Salau, former Ag. Vice Chancellor Prof. T.I. Raji, Prof. B.B. Adeleke, and Prof. M.L. Nasssar.

My very sincere and hearty appreciation to Prof. Wale Omole, OFR, eminent scholar, and famed University Administrator; Pro-Chancellor and Chairman, Governing Council, LAUTECH, and Hallmark University, Ijebu-Itele and Chief (Dr.) Mrs Leila Fowler, MFR, consummate educationist and legal luminary; Most. Rev. (Prof) Adebayo D. Akinde, renowned scholar and Archbishop of Ecclesiastical Province of Lagos and the Lord Bishop, Diocese of Lagos Mainland and Prof. & Prof.(Mrs). Adeniyi Osuntogun for their mentorship, support, and prayers.

I am indebted to my fathers' in the Lord, Bishop B. Amusan, the Lord Bishop of Oyo North Diocese, Bishop J.A. Ajetunmobi; The Lord Bishop of Ibadan South Diocese, Provost Rotimi Oludipe, Ven, (Engr) K.A. Aremu, Canon Ogundipe, Revds Peter Olujinmi, Adekola, Adegoke Pastor F. Oloruntimilehin and other current Priests at Ibadan South Diocese and all members of Young Men Christian Association (YMCA), Young Women Christian Association (YWCA), Christ Church, Mapo, Ibadan for their love, and prayers.

The current Vice Chancellor, Prof. Adeniyi Gbadegesin came to LAUTECH at a most difficult time. We all owe you gratitude for ensuring restoration of peace and amity on Campus after the last ownership crisis. Your activities and administrative acumen have encouraged the continued sustenance of LAUTECH as a centre of excellence and I wish you continued success and good health. Your friendship and that of your amiable wife over the years is equally appreciated. Thank you for accepting to build a new Central University Research Laboratory for this University.

I also thank all Professors and members of staff of Department of Pure and Applied Chemistry and Faculty of Pure and Applied Sciences for their friendship and support. My appreciation to all staff of LAUTECH, The Polytechnic Ibadan, University of Ibadan, University of Ilorin and Hallmark University who supported me in my various administrative positions. I salute the following administrators for tolerating a Scientist who believes nothing is impossible, for spending long hours at work and for been valuable drivers of our successes during my administrative assignments; Mrs. O.O. Oloke, T.O. Osundina, O. Oguntunde, and Messers F.O. Adebisi, S.L. Adefemi, A. Ajibesi, O. Oyerinde, O.O.I. Oyetunji, A. Odesola, Paul Akanbi, G.O.D. Olojede, Engr. S.O. Oke, Dr. N.O. Adebayo, late Mr. T.R. Ayanwale, and late Mrs. Olajumoke Alao and others too numerous to mention for their love and support.

I also want to express my appreciation to my brother and friend Mr. Adekunle Ogunesan, Managing Director Adesesan Graphics, my publisher for coming to my rescue throughout my administrative assignments when urgent work need to be in press even without notice including this lecture.

The greatest joy of today belongs to my former doctoral students and research collaborators Prof. I.O. Adeoye, Prof. M.A. Oladipo (former Heads of Department (HOD) of P/A Chemistry), Prof. O.O.E. Onawumi (current HOD, PAC), Dr. O.O. Osowole, Dr. F.A.O. Adekunle, Dr. B. Semire (all Readers/Associate Professors), Dr. O.I. Ibrahim and Dr. A.I. Adeagbo for their understanding and patience. I am sure you are very proud of our modest achievements and contributions to chemical literature. I am equally grateful to all my former students at the Bachelors and Masters level in various countries.

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(i) My paternal grandmother *aka* 'Mama Segun'; Mama Rebecca Morenike Odunola

(ii) My brother; Mr. Oluseye Odunola

(iii) My father in law; Papa Samuel Folorunso Osowole

Thank you all for listening and God bless.

*When I am down and oh my soul so weary*

*When troubles come and my heart burdened be*

*Then I am still and wait here in the silence*

*Until you come and sit a while with me*

*You raise me up so I can stand on mountains*

*You raise me up to walk on stormy seas*

*I am strong when I am on your shoulder*

*You raise me up to more than I can be.*

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