UNIVERSITY OF PORT HARCOURT

CHEMISTRY, keeping Nigeria and the world apart

An Inaugural Lecture

By

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MAPHA, FICCON

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DEDICATION

This work is dedicated to the memory of my late grandfather Eze Ideyi Uzoukwu Achum, whom I never knew. Though an illiterate, had thought it wise to send my own father among his twelve children, to school in the 1940s to become a Stenographer, who in turn sent me to school to become a Professor.

ACKNOWLEDGEMENT

I must begin by thanking the Almighty God most sincerely for granting me safe passage through the vicissitude of life to see this day, reinventing me with excellent health. May I express my appreciation to my parents Mr Ignatius Ekeyeekwute Uzoukwu (Adindu ana Ekwu) and Mrs Agnes Nwaikpeghe Uzoukwu (Oji Ugo) (Nee Nwadike), both of whom are now late for taking good care of me and sending me to school. I thank my late auntie Mrs Agnes Nwailojo Okeke and my siblings, Bernice, Dorothy (late), Grace, Nwanneka and Chukwudumeme for all their support and trust. I wish to express my immense gratitude to The Right Honourable Dr A A Nwafor-Orizu, former President of Senate and Acting President of the Federal Republic of Nigeria and his wife Mrs Ndonnwa Nwafor-Orizu, both of whom are also late for their intervention that lead to my training at National Secondary School Nnewi and also residing with them, at the very moment my parents cannot afford to send me to a Secondary School. I owe a deep sense of appreciation to my wife Ifeoma and children Soloudo, Ndonwanne and Onwenuzitelu for their love, support, patience and understanding going through the rough terrain of an academic.

The constraint of time and space will only permit me to show appreciation to a handful of people and organizations: my primary school teacher Mr Norbert Anagbogu; Professor Emmanuel C Okafor of the Department of Pure and Industrial Chemistry, University of Nigeria who was both my PhD thesis supervisor and mentor. The Alexander von Humboldt Foundation Germany for award of Research Fellowship on three different occasions and the International Foundation for Science Sweden for their support that contributed to some of the results that would be presented in this lecture. The students and staff of the Department of Pure and Industrial Chemistry, the Faculty of Science and Management of the University of Port Harcourt for their contribution to my life and career. A long list of friends, colleagues, mentors, benefactors and formators which cannot be contained in this lecture I say a big thank you.

Finally I would like to thank the Vice Chancellor of the University of Port Harcourt and the University Administration for making it possible for me to present the inaugural lecture of today and you the audience I also thank you for your attention.

CHEMISTRY, keeping Nigeria and the world apart

The Vice Chancellor,
Deputy Vice-Chancellors,
Registrar and other Principal Officers,
Provost College of Health Sciences,
Deans of Faculties,
Distinguished Professors and Scholars,
Great Students of Unique Uniport,
Distinguished Guests,
Ladies and Gentlemen.

1.0 INTRODUCTION

1.1 Preamble

Mr Vice-Chancellor, Sir it is with a deep sense of humility that I present the 73rd Inaugural Lecture of the University of Port Harcourt and I thank you most sincerely for the opportunity given me to do so. Prof Christopher Ejizu (2008), quoting Professor Chris Nwodo (2002), noted in the 59th Inaugural Lecture that 'an inaugural lecture in the Academy is meant to be a special occasion in which a new Professor is introduced not to a new job, but to a new rank, to his professorial chair' (C.S. Nwodo 2002). I also share some of the sentiments presented in that erudite lecture explaining what lead to many professors presenting their inaugural lectures late due to some reasons highlighted in that lecture. I have been a Professor for some 5 years now and I thank you once more for affording me the opportunity of mounting this academic rostrum relatively early.

1.2 Basic Concepts

Mr Chairman, this inaugural lecture is rooted in chemistry and I shall try to carry everybody along particularly members of the audience whose background in chemistry is on the periphery. Chemistry is the scientific study of the changes that occur when substances interact with one another (Manilla, et al 2001). Put in a layman's language:

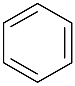
$$A + B \rightarrow C$$

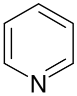
Where A and B are the interacting substances, symbolised by +, to give a substance(s) C that is totally different from both A and B physically and chemically. This definition, as simple as it may be has already showed some signs of the complications embodied in Chemistry as a huge and well developed area of science. Because chemistry is the science of the consequence of changes resulting from the process of interaction the word chemistry has been found to be a suitable term used in many sphere of human activities ranging from science, humanities to arts. For this reason one finds the word chemistry in politics to explain the mechanism that leads to changes that occur when bad policies are imposed on the people. In our social life it is the chemistry of the interaction between two individuals that are in love that is consumed in a love affair. And none of these two processes is as simple as $A + B \rightarrow C$ and yet it is $A + B \rightarrow C$. It is the chemistry of the interaction of musical vibration on the ear that results in a dance. When a person is dancing when there is no obvious source of music then the person is seen by an onlooker, simply as someone who has gone mad. But if in all consciousness it is known that the person is not mad then an Igbo proverb has it that somebody is playing the music for him from somewhere inside the bush. Simply put, chemistry is complete in all ramifications as long as there is interaction between two or more objects or events.

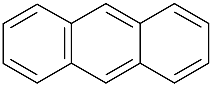
At some point we all encounter chemistry to varying extent in addition to the fact that there is nothing around us that is not chemistry, ranging from our daily individual encounters with each other to minute events such as the war of eyes meeting eyes, the food we eat, the cloths we wear, our hygiene, our cars, the air we breathe, beauty and fashion, music and the person who responds to the musical vibration, politics and the society. Hence chemistry is everywhere. So we are all at any point in time in a chemistry class but with few Chemists amongst us. Thus for the Chemists chemistry has been divided into various scientific areas that are all equally well developed, highlighted below.

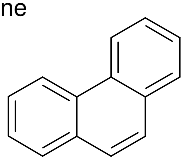
1.2.1 Organic Chemistry: This is the chemistry of carbon and its compounds. In this branch of chemistry we study the synthesis, characterization and application of compounds that have been classified as hydrocarbons and hydrocarbon derivatives. Examples include,

(a) Alkanes: C_2H_6, C_3H_8, etc.
(b) Alcohols: CH_3CH_2OH (kie kie), $CH_3CH_2CH_2OH$, etc .
(c) Ketones, aldehydes, amines and carboxylic acids, etc.
(d) Aromatics and their derivatives:

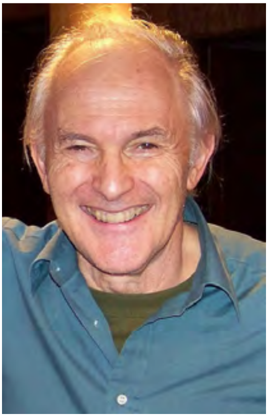

benzene


pyridine


Anthracene


Phenanthrene

For clarity the hydrogen atoms in the above compounds have been omitted. The basis of these compounds is that carbon atom must arrange itself in an environment surrounded by 4 points of attachment. Many chemists have exploited this property of carbon and have synthesised giant molecules or macromolecules and Harold Kroto (1985) isolated a substance composed of carbon bonded to one another forming a 60-carbon atom ball called fullerene for which he and two other persons were awarded the 1996 Nobel prise for chemistry.



Prof Harold Kroto (1939 date)

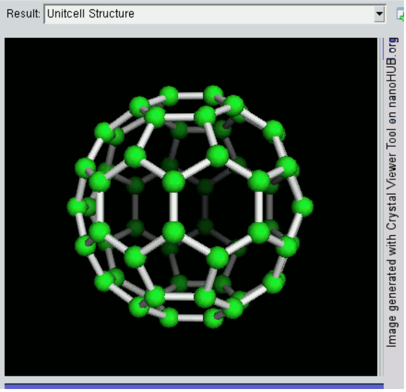


Fig 1 Fullerene C_{60}

Fullerene is a form of carbon allotrope composed entirely of carbon atoms arranged in a hollow sphere as shown in Fig 1. Derivatives of this compound have been ingeniously synthesised and have found very useful applications in material science, electronics and nanochemistry.

1.2.2 Inorganic chemistry: This is the branch of chemistry that deals with elements generally grouped as representative elements other than those covered under the organic chemistry of carbon. It studies the chemistry of metals e.g. iron Fe, nickel Ni, copper Cu etc, non-metals e.g. oxygen O_2, sulphur S, nitrogen N, and metalloids which are elements that possess both metallic and non-metallic properties e.g. silicon, Si, germanium Ge, which is the backbone of the silicon and electronic industry. Some of the compounds encountered domestically are:

sodium chloride (common salt) NaCl, calcium sulphate ($CaSO_4.2H_2O$) (gypsum used for making plaster of Paris), sodium sesqui-carbonate (akanwu) ($Na_2CO_3.NaHCO_3.2H_2O$), calcium carbonate (lime stone) ($CaCO_3$), calcium oxide (quicklime) (CaO), potassium nitrate (saltpeter) KNO_3), potassium permanganate (permanganate potash) ($KMnO_4$), potassium hydroxide (caustic potash) (KOH), etc.

These are simple examples of Daltonic compounds or compounds in which the atoms are related to each other in the formula in simple integral ratios described as stoichiometry. When the formula is non-Daltonic or non-stoichiometric the atoms may exit as fractions in a compound or in ratios that don't conform to the Daltonic theory of an atom. They are described as interstitial compounds.

Examples are $Fe_{0.95}O$, Fe_7S_8, Fe_9S_{10}, $WO_{2.95}$, YBa_2Cu_3O

They have been very useful in the ceramic industry for designing ballistic armed vests, protection of military cockpits of planes, glass, electronic, construction of super metal alloys used in aerospace engineering, super jet engines, turbine blades, etc.

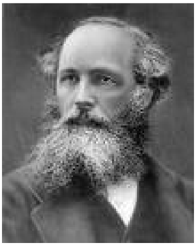
1.2.3 Physical Chemistry: This is the branch of Chemistry that applies mathematical concepts and methods in Physics to study the properties of substances and chemical processes. This is the tool with which the language of Chemistry is spoken. It is that branch of chemistry that enable Chemists present any aspect of Chemistry in its essence, its debt and rationale. Little wonder that may great names in chemistry and indeed science are linked to various sub-units of Physical Chemistry such as Theoretical Chemistry, Thermodynamics, Electrochemistry, Quantum Chemistry etc. They include people like Albert Einstein the German Physicist and Nobel Price winner in Physics who explained the basis of photoelectric effect in photoelectric materials using the concept of quantization of energy; Germain Henri Hess (1802 to 1850) the Russian Chemist who made great contribution in the field of Thermochemistry and discovered the laws guiding the heat of formation of compounds; Jacobus Henricus van't Hoff (1852 to 1911) the Dutch Physical Organic Chemist who in 1901 won the first Nobel Price in Chemistry as a result of his work in the field of Thermodynamics; Ludwig Boltzmann (1844 to 1906) the Austrian Physicist who has made tremendous contribution to statistical mechanic and thermodynamics and the kinetic theory of gases; James Clerk Maxwell (1831 to 1879) was a Scottish Physicist and Mathematician who showed that electricity, magnetism and light are all phenomena arising from the same process; Michael Faraday (1791 to 1867) an English Chemist and Physicist who made tremendous contribution in electromagnetism and electrochemistry, etc.

Albert Einstein 1879 to 1955

Germain Henri Hess (1802 to 1850)

Jacobus Henricus van't Hoff (1852 to 1911)


Ludwig Boltzmann (1844 to 1906)


James Clerk Maxwell (1831 to 1879)


Michael Faraday (1791 to 1867)

1.2.4 Analytical Chemistry: This is the branch of Chemistry that applies physical and chemical concepts in the detection and estimation of the amount of a substance in a sample. This branch of Chemistry is also involved in the development of the detection and estimation techniques and catalogues of research work generated from this area can be sited in learned journals such as Polyhedron, Frasier Journal of Analytical Chemistry, Radiochimica Acta, Analytical Letters, Separation Technology, Microanalysis, Solvent Extraction and Ion Exchange, Supramolecular Chemistry, etc. My area of specialization is Analytical-Inorganic Chemistry.

1.2.5 Analytical-Inorganic Chemistry: This sub-unit of Analytical Chemistry is devoted to the development and application of chemical and physical concepts in the analysis of inorganic species. To be able to make an impact in this field one needed a sound knowledge of Coordination Chemistry and metal-ligand synthesis which are rooted in basic Inorganic Chemistry; and a core analytical chemistry process such as Separation methods. The aspect of separation method that is of interest to me is liquid-liquid extraction. Hence an Analytical-Inorganic Chemist is expected to be grounded in Inorganic Chemistry to be able to apply chemical and physical concepts in the development of detection and quantification techniques for Inorganic species. For instance the identification of species may involve the determination of spatial arrangement of constituent species of an analyte in two or three dimensions using techniques of structural analysis. In this aspect a sound knowledge of Coordination Chemistry becomes very paramount.

2.0 COORDINATION CHEMISTRY

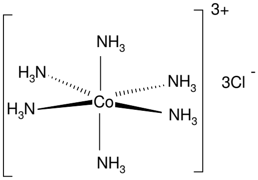
This is the branch of Chemistry that studies bond formation between atoms and their spatial arrangement around a central atom, particularly when the central atom is a metal, after an interaction with ligands to form complex species.

In this field Mr Vice Chancellor we have made contributions to some Journals that are very much respected globally in the field of Chemistry and they include, Inorganica Chimica Acta, Polyhedron, Spectrochimica Acta, Acta crystallographica to name just a few arising from our modest work on the synthesis and characterization of over 300 new metal complexes and over 20 ligand species covering bidentate and tetradentate diketones and Schiff bases. These work were carried out in laboratories of the Departments of Chemistry at the University of Nigeria Nsukka; University of Port Harcourt, Port Harcourt; University of Sussex Brighton England; University of Hannover Germany and Technical University Dresden, Germany at various times spanning over a period of 25 years.

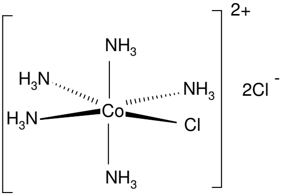
The emergence of Coordination Chemistry as a special area in Chemistry is attributed to the work of Alfred Werner a Swiss National who in 1893 propounded the basis of coordination theory that solved the mystery of the structure of metal complexes for which in 1913 he was awarded the Nobel Prize for Chemistry; becoming the first person to win a Nobel Prize in Inorganic Chemistry.

Alfred Werner 1866 – 1919

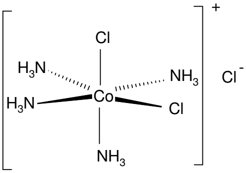
His work was a tremendous contribution to advancement in the chemistry of metal complex species at that time because it was done at a time of the non-existence of x-ray diffraction as tool for structural elucidation. Werner had enough insight at his time without x-ray diffraction data at his disposal to be able to recognise that a complex species has primary and secondary valences. For the three chloro species of the aminocobalt trichloride compounds $CoCl_3.6NH_3$, $CoCl_3.5NH_3$ and $CoCl_3.4NH_3$ which he worked on, he deduced the following structures based on his postulated existence of primary and secondary structures revealed mainly through measurements of electrical conductivities of their solutions and isolation of their silver chlorides as follows:



CoCl$_3$.6NH$_3$

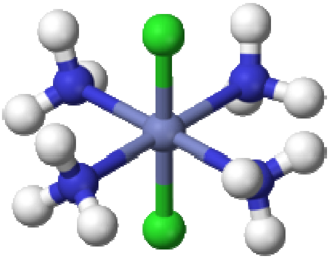


CoCl$_3$.5NH$_3$

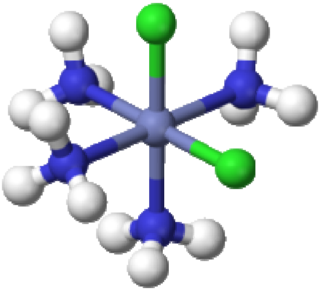


Co$_3$.4NH$_3$

He was also able to recognise two isomeric forms of the CoCl$_3$.4NH$_3$ complex and actually isolated the first compound with a non-carbon chiral centre.



Trans-Co(NH$_3$)$_4$Cl$_2^+$



Cis- Co(NH$_3$)$_4$Cl$_2^+$

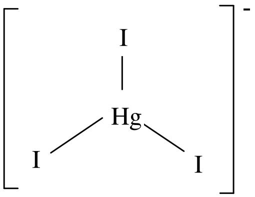
The compounds listed above are actually characterised as having a coordination number of six. Coordination number is the number of bonding sites around a central atom that are occupied by atoms. Werner was able to recognise the influence of coordination on the final structural orientation of metal complexes as exemplified by some of the complexes presented below.

2.1 Coordination number of two: Two bonding sites around a central atom occupied by atoms.

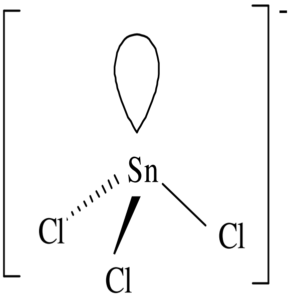
$$\left[H_3N - Ag - NH_3\right]^+$$

Diammine argentum(I)
Linear

2.2 Coordination number of three: Three bonding sites around a central atom occupied by atoms.

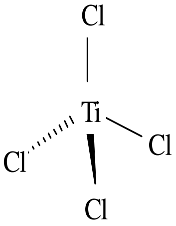


Triiodo mercury(II)
Triangular

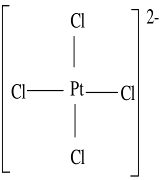


Trichlorostanate(II)
Pyramidal

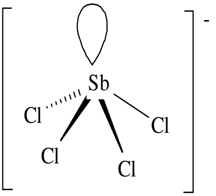
2.3 Coordination number of four: Four bonding sites around a central atom occupied by atoms. Some of the structures associated with this coordination number are:



Titanium tetrachloride
Tetrahedral

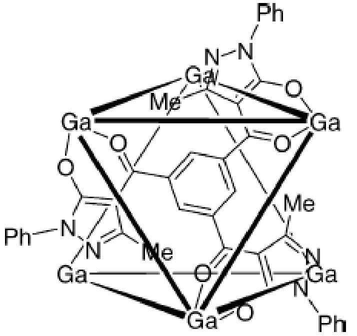


Tetrachloroplatinate (II)
Square planar



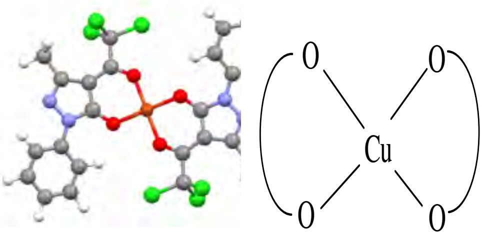
Tetrachloroantimonate (III)
Tetrahedron

This included some exotic superimposed tetrahedral complex arrangement reported by Marchetti et al 2005 for gallium complex species with pyrazolonato backbone.



Gallium pyrazolonato complex species

We have isolated Cu(II), Mn(II), Zn(II), Ni(II) pyrazolonate complexes that are square planar in configuration (Uzoukwu, 1990, 1992, 1993) as shown by the molecular modelled structure (Fig 2) of Cu(II) complexes of bidentate pyrazolones.



Simplified form of the structure

Fig 2 Bis(1-Phenyl-3-methyl-4-trichloroacetylpyrazonato) copper(II)

We have also observed similar structural feature in the Cu(II) polymethylene tetradentate pyrazolonate complexes (Uzoukwu, 1998) with hand catcher configuration suitable for configuring ladies hand bag (Fig 3).

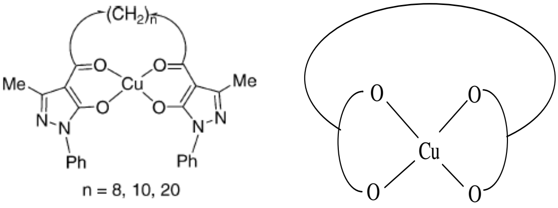
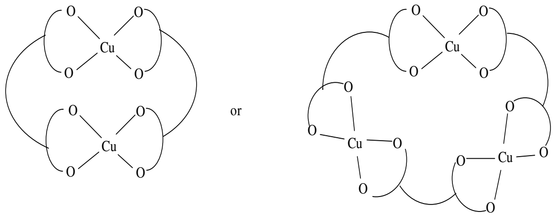


Fig 3 1-phenyl-3-methyl-4-sebacoylpyrazonatocopper(II)

Our work went further to propose possible macromolecular structures shown in Fig 4 of the complexes similar to many macromolecules already synthesised by Chemists.

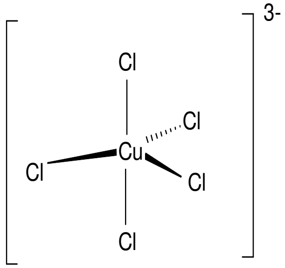


etc

Fig 4 Possible macromolecular structures of 1-phenyl-3-methyl-4-sebacoyl-pyrazonatocopper(II)

Supramolecular Chemistry has further shown that species with long polymethylene chains such as the bis-sebacoyl and bis-adipoyl pyrazolone metal(II) complexes that we were able to isolate are capable of self assembly to knotanes, catenanes and rotaxanes (Lukin and Vogtle, (2005)). That is an area of research currently going on in most advanced countries.

2.4 Coordination number of five: Five bonding sites around a central atom occupied by atoms. Some of the structures associated with this coordination number are:



Trigonal bipyramidal Pentachlorocuprate(II) ion

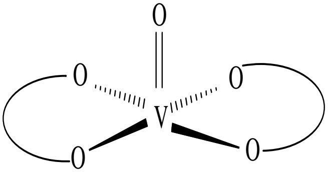
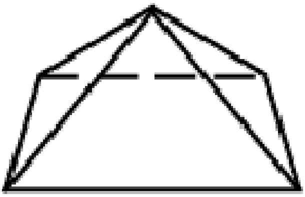


Fig 5
Square pyramidal
Bis(1-phenyl-3-methyl-4-acetyl pyrazonato) vanadium(IV)

In the course of our work on 4-acylpyrazolones we were able to isolate and completely characterise the square pyramidal vanadyl complex species presented in Fig 5. A combination of various spectral techniques shows that the vanadyl complexes are actually distorted square pyramidal structures with stereochemically differing (Uzoukwu, 1992b) C=O-V bonds as a result of the presence of bridging vanadyl(IV) groups (Fig 5a).



Square pyramid

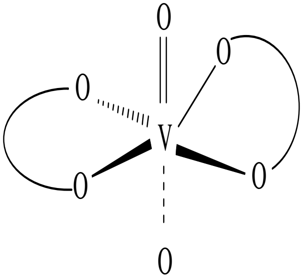


Fig 5a Distorted square pyramidal structure

On the contrary the five coordinated vanadyl(V) complexes formed distorted trigonal bipyramidal (Uzoukwu, 1991, 1998) structures (Fig 5b).

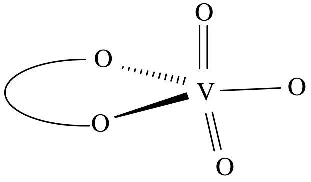
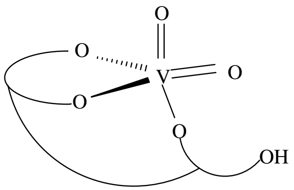
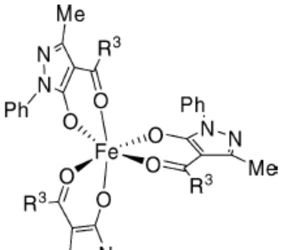


Fig 5 b Distorted trigonal bipyramidal



With polymethylene pyrazolone moiety (Uzoukwu, 1998)

2.5 Coordination number of six: Six bonding sites around a central atom occupied by atoms. Many metal dioxy species interacting with bidentate ligands give rise to complex species with CN6 configuration. Among species isolated during our research work included the Fe(III) (Okafor and Uzoukwu, 1992) complex that exhibited regular octahedral configuration (Fig 6).



R^3 = Me, Pr

Octahedron

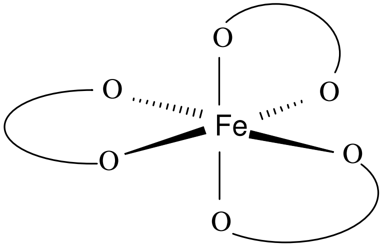


Fig 6 Octahedral Tris(1-phenyl-3-methyl-4-acetyl pyrazonato)iron(III)

Some exotic octahedral complex species (Fig 6a) similar to the distrontium hexakis((1-phenyl-3-methyl-4-acetylpyrazolonato) have been isolated by Marchetti et al in 2005.

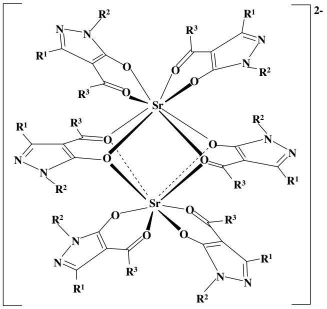


Fig 6a Distrontium hexakis((1-phenyl-3-methyl-4-acetylpyrazonato)

An ORTEP plot of the tin(IV) dichloropyrazolonato (Uzoukwu, et al 2001) isolated shows the presence of 3 optical isomers (Fig 6b). Optical isomers are species that are mirror images of one another as shown by the tin(IV) dichloropyrazolonato (Uzoukwu, et al 2001) that was isolated.

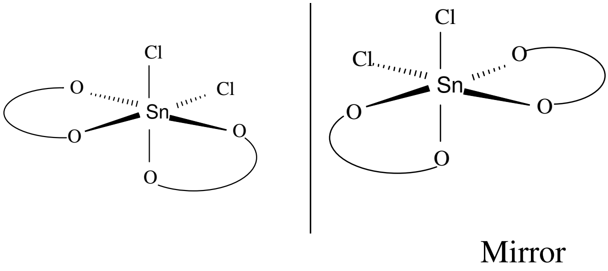
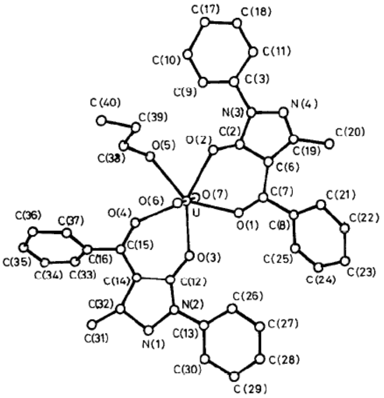
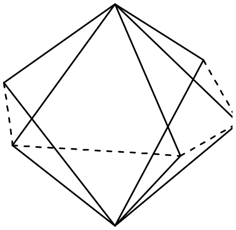


Fig 6b Optical isomers of Tin(IV) Dichlorobis(1-phenyl-3-methyl-4-acetylpyrazonato)

The uranyl bispyrazolonato (Okafor, et al 1990; Uzoukwu, 1990b, 1998) rather than crystallizing as an octahedral complex appeared with a pentagonal octahedral configuration (Fig 6c) which was characterised spectroscopically as due to formation of adduct species.



Uranyl Butyrylpyrazolonate propanol adduct
Monoclinic with a space group *Cc*



Pentagonal Octahedron

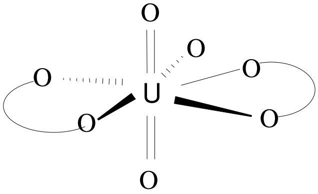


Fig 6c Simplified pentagonal octahedral structure of the above complex

Similarly molybdyl(II) complexes (Uzoukwu, et al 2001) were isolated as octahedral species and as a trichloro substituted dioxomolybdenum(V) complex which is a very unusual complex species because of the existence of trichloro substituent at a beta position to the central metal ion, rather than on the central metal ion itself. This is an indication that the complex is not an adduct but a trichloro derivative of dioxomolybdenum(V) pyrazolonato and the first time such unusual complex formation has been reported.

Metal complexes with binuclear (Uzoukwu, et al 2000b) octahedral configuration (Fig 6d) have been propounded and complexes with mixed tetrahedral and octahedral centers in the same crystal lattice (Fig 7) have been isolated and reported (Uzoukwu, et al 1996; Uzoukwu and Adiukwu, 1997).

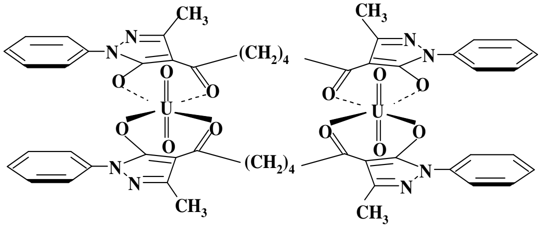


Fig 6 Binuclear octahedral Uranyl polymethylenepyrazolonato

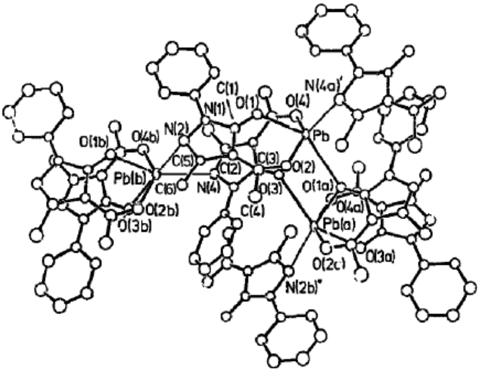


Fig 7 Bis(1-phenyl-3-methyl-4-acetylpyrazolonoato)lead(II) Monoclinic space group $P2_1$

Complexes with Coordination number of eight (CN8) have been isolated and have been characterized as square antiprismic (Fig 8) complexes and bicapped trigonal antiprismic (Fig 8a) complex (Uzoukwu and Adiukwu, 1997b) species.

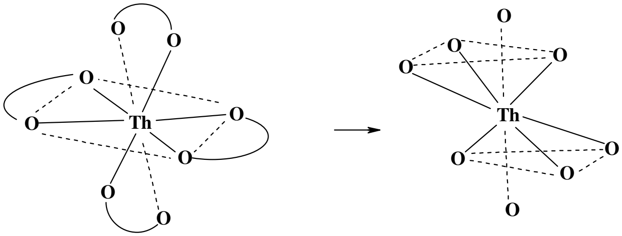


Fig 8 Bicapped trigonal antiprismic thorium (IV) 4-acylpyrazolonato

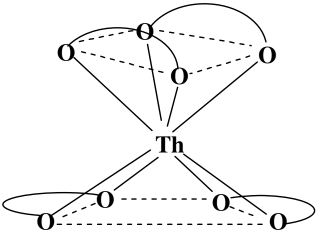


Fig 8a Square antiprismic thorium (IV) 4-acylpyrazolonato

3.0 LIGANDS

Ligands are species that contain at least a lone pair of electrons for donation to a cationic centre. Ligands are therefore very central in coordination chemistry, metal complexometry and Analytical-Inorganic Chemistry. Sir we have synthesised and contributed to the bank of new ligand species through the synthesis of the following ligands whose structures we have completely resolved through elemental analysis, ultraviolet-visible, Infra-Red, Proton-Nuclear Magnetic Resonance, Carbon-Nuclear Magnetic Resonance and x-ray diffraction spectrophotometries. They are (Figs 9 – 9e):

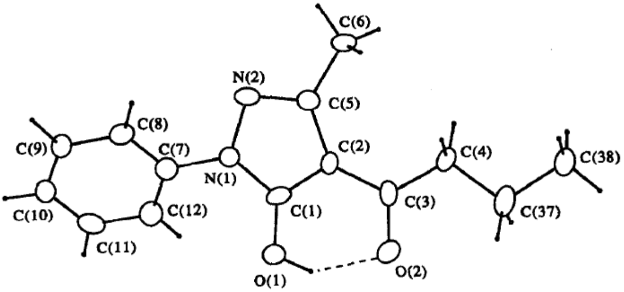


Fig 9 1-Phenyl-3-methyl-4-butanoylpyrazol-5-one (Okafor and Uzoukwu, 1992)
Orthorhombic space group *Pbcn*

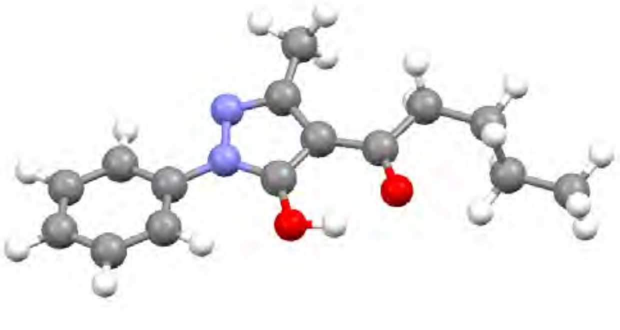


Fig 9a Molecular modelled structure of 1-Phenyl-3-methyl-4-butanoylpyrazol-5-one

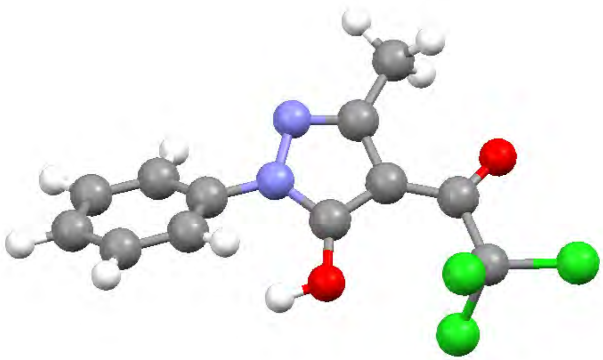


Fig 9b Molecular modelled structure of 4-Trichloroacetyl-5-methyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one

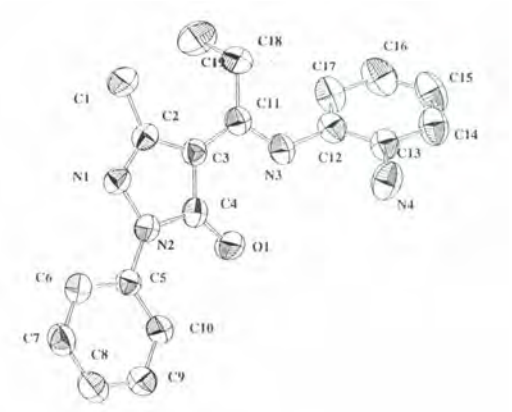


Fig 9c 1-(4-propanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) 2 aminobenzene (Uzoukwu, et al 2001b) Monoclinic space group $P12_1ln1$

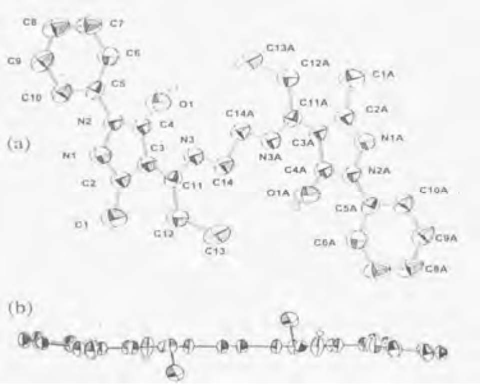


Fig 9d N, N'-Ethylenbis(4-propanoyl-2,4-dihydro-5-methyl-phenyl-3H-pyrazol-3-oneimine)
Triclinic space group $P\bar{1}$

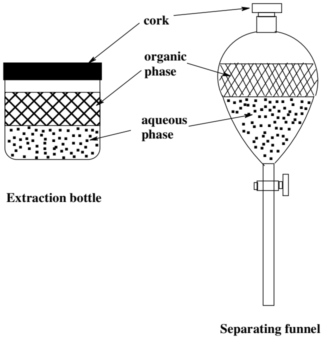
Fig 9e Molecular modelled structure of 4-Acetyl-5-methyl-2-phenyl-1,2-dihydro--3H-pyrazol-3-one hydrate (Uzoukwu, et al 2000)

We have shown that any derivative of 4-acylpyrazol-5-one can be qualitatively identified as an alkyl, aromatic or trihalo derivative based on their uv-visible spectral characteristics (Uzoukwu, 1995).

4.0 SOLVENT EXTRACTION

This is a separation method in which at least a solvent phase is involved as one of the phases involved in the separation process. Hence we have liquid-liquid, liquid-solid and liquid-gas solvent extraction processes. My area of specialization is liquid-liquid extraction.

Liquid-liquid extraction is an extraction technique that involves two immiscible liquid phases that are in contact with each other in which the solute of interest distributes its self from the aqueous phase to the organic phase under the condition created for the distribution process. In such a situation conditions can be created such that a substance of interest in the midst of other undesirable substances can distribute preferentially from the aqueous substrate to the organic extractant. At the end of the extraction process the substance of interest (in this case a metal ion) is separated from a mixture of metal ions. Interestingly very simple apparatus such as separating funnels or extraction bottles (Fig 10) are needed.



Extraction bottle

Separating funnel

Fig 10 Extraction apparatus for liquid-liquid extraction

As simple as these apparatus may be Mr Vice Chancellor it may interest the audience to know that these were the sort of implements and technique used by the Americans at the first stage of their research for separating pure forms of the radioactive materials used for making the 1st recorded nuclear bomb. These tools and techniques guided by the same principles are still being used today for the separation of hazardous radioactive isotopes from wastes of nuclear plants (Schulz, et al, 1987; Egorov, et al, 1992; Moyel, et al, 2005) for safe storages. Although a lot of innovations have been introduced the basic concepts in the separation process still remains the same. That is, for two immiscible liquid phases the distribution ratio D of the concentration of the solutes in all forms in the two liquid phases remain constant under a particular experimental condition.

$$D = \frac{\sum C_{or}}{\sum C_{aq}}$$

Where $\sum C_{or}$ = total concentration of solutes in organic phase and

$\sum C_{aq}$ = total concentration of solutes in aqueous phase

The experimental conditions that can be varied for the extraction process are temperature, pH, salt, acidic anions, auxiliary complexing agents, kinetic factors, type of organic phase and changes in solvents. Manipulation of one or more of the above enlisted experimental conditions can lead to the separation of a metal ion from a mixture of metal ions, whether it is radioactive or non radioactive, precious or just metal of ordinary industrial interest. Sir by manipulating some of the above conditions during our over 25 years work on pyrazolone and pyrazoloimine derivatives and their metal complexes we have been able to device methods for,

-the separation of Uranium(VI) from Iron(III) (Okafor and Uzoukwu, 1990),

-separation and spectrophotometric analysis of Iron(III) (Uzoukwu and Jack, 1993) and Vanadium (V) (Uzoukwu and Oforji, 1993),

-separation of chromium(VI) and molybdenum(VI) from mineral acids (Uzoukwu and Nwachukwu, 1994; Uzoukwu and Ukegbu, 1997),

-separation of Iron(III) from vanadium(V) (Uzoukwu and Etesin, 1995),

-separation of uranium(VI) from vanadium(V) (Uzoukwu, et al, 1998b),

-separation of Cu(II) from a mixture with Nickel(II) and Zinc(II) (Uzoukwu and Mbonu, 2005), etc.

Kinetic studies with bispyrazolones (Uzoukwu, et al, 1998c) have shown that the rate of extraction of uranium(VI) is proportional to the reciprocal of hydrogen ion concentration $[H^+]$, while that of mercury is proportional to the reciprocal of the square root of hydrogen ion concentration $[H^+]$ as shown below:

$$-\frac{d[UO_2^{2+}]}{dt} = k_f[UO_2^{2+}][H_2SP][H^+]$$

$$-\frac{d[Hg^{2+}]}{dt} = k_f[Hg^{2+}][H_2SP][H^+]^2$$

5.0 SUPRAMOLECULAR CHEMISTRY

Simply put, this is the chemistry of supramolecules. Supramolecules are products that arise from intermolecular self-assembly of small molecules or molecular subunits. Hence supramolecules are species beyond molecules. This is the area of current interest in the development of ligand metal interaction where many of our contemporaries overseas have left many of us behind in the field of organic, inorganic and applied chemistry. Simply put, we are still trying to grapple with the Old Testament while they have gone far with the New Testament. This is because majority of us are still involved with metal ligand reactions involving covalent bond formation through metal ligand interaction as a result of the displacement of hydrogen ion from a ligand (Okafor, et al, 1993; Okafor and Uzoukwu, 1993; Uzoukwu, 1993b; Uzoukwu, et al, 2000b, 2004) as shown in Fig 11 for a complexation reaction between an acylpyrazolone and a divalent metal M.

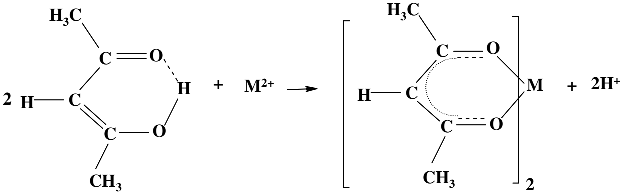


Fig 11 Complexation reaction between acylpyrazolone and metal M^{2+}

Colleagues in the same field overseas are now laying more emphasis on non-covalent interaction as a major sphere of ligand metal interaction. We are used to extraction of metal ion species from aqueous phases through covalent bond formation, but the latest concepts on non-covalent bond interaction have lead colleagues to be exploring the extraction of metal ions in addition to extraction of anionic species such as chloride, fluoride, nitrate, chromate, technetate, rhenate, sulphate, phosphate etc. through non-covalent bond interaction, a phenomenon that is known to be taking place in living organisms. The consequence of this is that whenever we visit Europe after a gap of about 5 years we discover that within this short span of time, one is already outdated with both the latest development in Chemistry and the latest technology with which to study it. One would always discover that the molecular modelling package known to him 5 years before is no more relevant having being replaced by more efficient and more sophisticated packages such that one needed to be retrained to come on board. The instruments one used 5 years before are now packed away for disposal somewhere having being replaced by more modern equipment.

Self assembly in supramolecules is facilitated by non-covalent interactions such as hydrogen bonding (Beijer, et al 1998), weak intermolecular van der Waals interaction (Lehn, 1988; Bravo, et al, 1998), π-π interaction, hydrophobic interaction and electrostatic interactions. *Hydrogen bonding* is a dipole-dipole non-covalent interaction between a hydrogen atom and another heteroatom such as O, N or F within or outside a molecule, giving rise to intramolecular and intermolecular (Fig 12) hydrogen bondings respectively.

Fig 12 Intermolecular hydrogen bonding

Pi-pi interaction is a non-covalent interaction that leads to stacking of aromatic moieties due to the presence of π-orbitals in a system. Numerous examples could be found in biochemical systems of amino acid, phenylalanine, tyrosines, etc. Hence, π-π interactions are very important interactions in polycyclic aromatic supramolecules as illustrated by two differently coloured molecules of Fig 13.

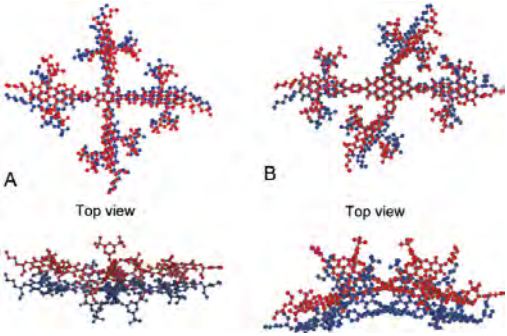


Fig 13 Red and Blue molecules illustrating π-π interactions from top view

A better view of arrangement resulting from π-π interactions is shown by the side view of molecules shown (Fig 13a) below,

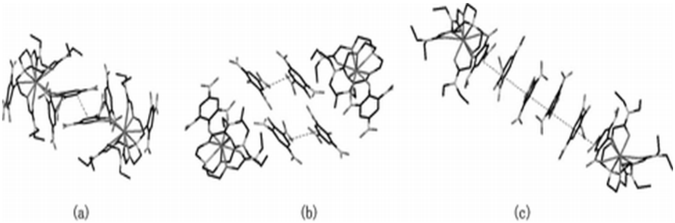


Fig 13a Pi-pi interaction as seen from a side view of the molecules

The fascinating thing about molecular self assemble is that the molecules tend to organise themselves in a manner that optimises their size creating a balance between intermolecular interaction and spatial arrangement in a pre-determined fashion. The result is the emergence of fascinating supramolecular designs and archtecture such as the *Borromean rings* (Fig 14). In the Borromean rings (Chichak, et al 2004) three molecules are interlocked into rings in such a way that when any one of the molecules is removed the other two molecues are automatically unlocked.

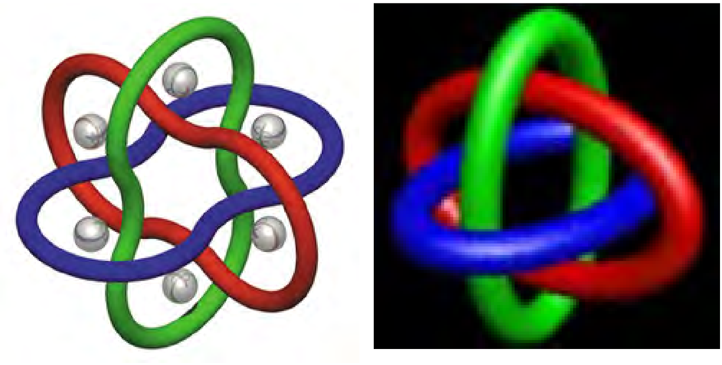


Fig 14 Borromean rings

Fig 14a shows a borromeate synthesized from a combination of 2,6-diformylpyridine, 2,2’-bipyridine containing diamine, templated with zinc acetate giving the structure that has been graphically shown below.

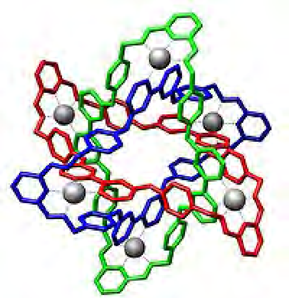


Fig 14a Structure of a borroomeate

Mechanically interlocked molecules as seen in catenanes (Fig 15) (these are mechanically interlocked molecular architecture consisting of two or more interlocked macrocycles).

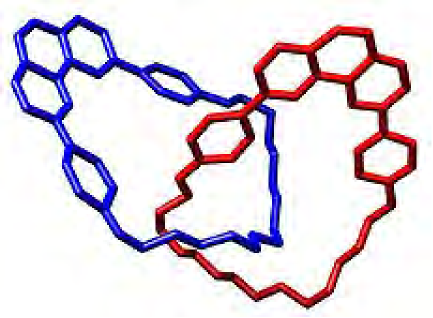


Fig 15 Structure of a catenane

Knotanes (Fig 16) (these are mechanically interlocked molecular architecture consisting of two or more molecules interlocked in a molecular knot).

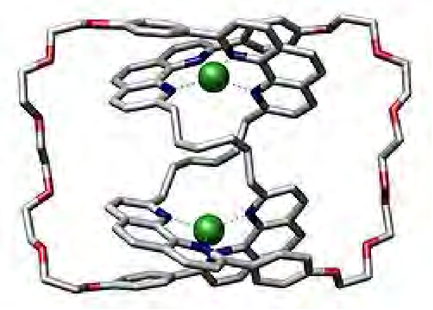
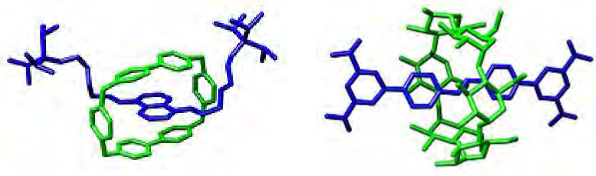


Fig 16 Structure of a knotane

Rotaxanes (Fig 17) (these are mechanically interlocked molecular architecture consisting of one molecule threading through another molecule).

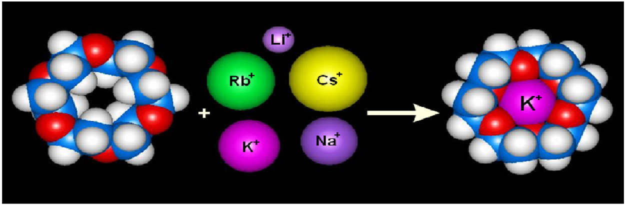


α-Cyclodextrin
macrocyclic (Stanier,
et al 2001)

Fig 17 Structure of a rotaxanes

5.1 Pre-selectivity in host-guest relationship

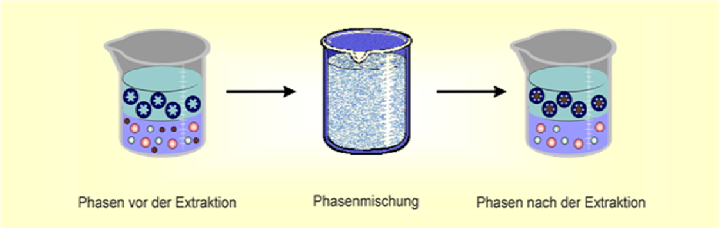
This is demonstrated in Fig 18 by the modelled interaction of a ligand in the extraction of potassium ion in the midst of other group I ions despite the fact that they all have identical reactivity with the same ligand.



Courtesy of Prof Karsten Gloe TU Dresden, Germany

Fig 18 Pre-selectivity in the extraction of K^+ in a mixture with group I metallic ions

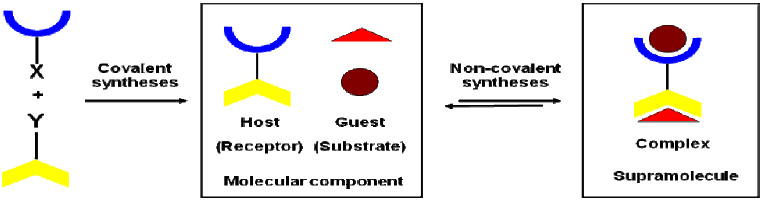
Hence the ability of molecular recognition plays very important role in solvent extraction involving formation of supramolecules as illustrated by the recognition of a species in the midst of other species by simple non-covalent interaction between the ligand and the desired guest. This technique has been used in nuclear waste clean-up where calixcrown (calyx[4]arene-bis(4-tert-octylbenzo-crown-6) has been used in a guest-host recognition for the separation of radioactive cesium-137 in a pool of nuclear waste (Moyer, B A. et al 2005) as illustrated by the solvent extraction process of Fig 18a.



Courtesy of Prof Karsten Gloe TU Dresden, Germany

Fig 18a Solvent extraction involving host-guest recognition

5.2 In molecular design



Courtesy of Prof Karsten Gloe TU Dresden, Germany

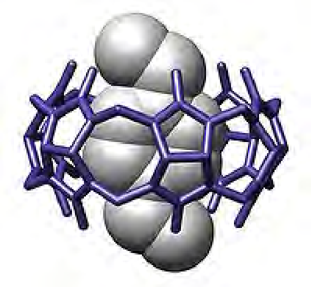
Fig 19 Sequence in molecular design

Molecular design utilizes the principle of pre-selectivity in host-guest relationship in producing intriguing molecular architecture as illustrated by Fig 19.

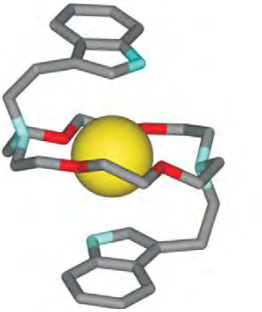
The ability of supramolecular involvement in the extraction of both cationic and anionic species has opened an interesting angle of the potentials of supramolecules because it helped throw much light into chemical processes in living organisms because supramolecules are very much involved in living processes leading to the ability of biochemical species to recognise and interact selectively and non-covalently with cations such as Mn, Fe, Se, Zn, Ca, Na and anions such as Cl^-, I^-, NO_3^-,PO_4^{3-}, etc in the midst of other ions in a predetermined fashion.

There is however a huge concern in supramolecular chemistry; that is in the ability of supramolecules to pre-determine the way they want to arrange themselves. The implication is that supramolecules and not humans, actually determine the kind of arrangement they would want to take up with the inherent properties, which could be either beneficial or devastating to the human race, and there is a fair change that this could happen any time in the history of man as long as we continue to manipulate molecules to get new products or in trying to understand nature without caution. So far supramolecular self assembly through synthesis, templating, solvent extraction, guest-host relationship and molecular recognition has given us properties that are beneficial to the human race. The question now is this, what happens if a newly synthesized supramolecular product self assembles its self to an arrangement that could wipe out the human race through a propagated chain of self assemble, particularly when the Chemist does not have much say in pre-determining the arrangement or the outcome of the arrangement of the supramolecules. It comes to reason that there are useful supramolecular arrangements which are the ones that are beneficial to man as seen in molecular recognition processes (Fig 20):

Host-guest processes



Molecular templating and encapsulation



Modelled structure of potassium complex of N,N'-bis(2-(3-indolyl)ethyl)-4,13-diaza-18-crown-6 reported by Lu W et al (2004).

Molecular encapsulation

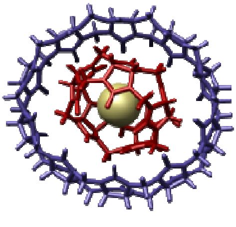


Fig 20 Molecular recognition processes

5.3 Mechanical molecular switches

In this case the ability of molecules to arrange themselves in a predetermined fashion has turned the molecules into potential application as molecular machines and switches when responding to some external stimuli. Murakami el al (1997) have synthesized a molecular shuttle based on rotaxane consisting of a cyclodextrin moving forth and back between two stations in the same supramolecules in response to external illumination of uv and visible light.

5.4 Nanochemistry and the emergence of nanotechnology

This is the branch of science that studies the synthesis and characterization of chemical species at the nano scale range. This new and emerging area is facilitated by the ability of self assembly of molecules into building blocks. Modelled formation of nanocapsule, nanofibre and nanotube (Fig 21 – 21b) by molecular self assembly involving molecules with hydrophobic alkyl chain and hydrophilic dendrimers fitting themselves into the end of a rigid segment to give intriguing molecular designs have been published in a review by Ryu et al 2008

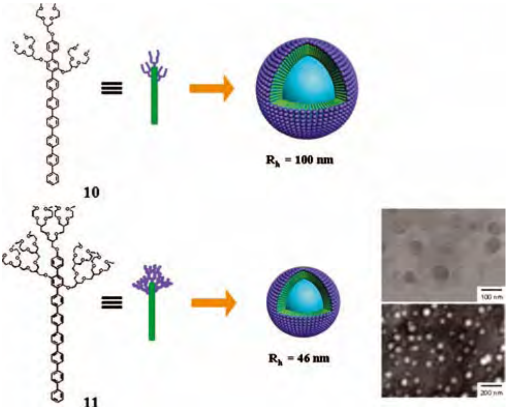


Fig 21 Modelled formation of nanocapsules (Ryu, et al 2008).

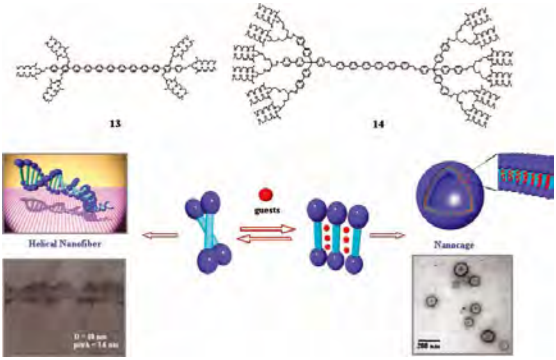


Fig 21a Modelled formation of a helical nanofiber and nanocage showing encapsulation of a guest in a nanocage. Note the formation of helical fiber similar to DNA (Ryu, et al 2008).

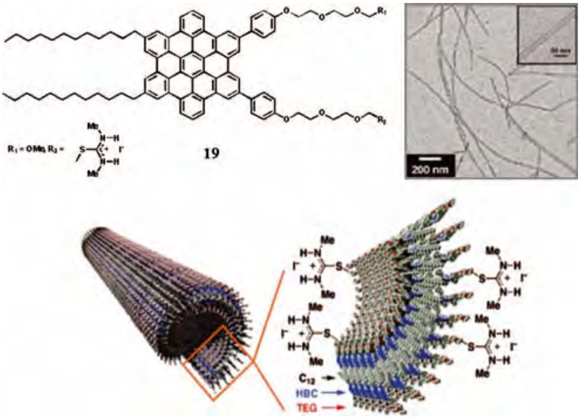


Fig 21b Modelled structure depicting a graphical formation of a nanotube (Ryu, et al 2008).

The above useful supramolecules implies that there may be retrogressive supramolecules, although not yet known, or perhaps known by those manipulating these molecules but have kept them as Top State secret. Could we just pause for a moment and imagine a situation where the supramolecules synthesized needed oxygen to self assemble and due to type do not need the human being to do so, provided that the core template has been put in place. A schematic diagram proposing the nature of a typical rotaxane (not yet in existence) which I named ‘*anaerobitizer*’ incorporating oxygen molecules in a propagating fashion during the process of self assembly may be pictured as shown in Fig 22.

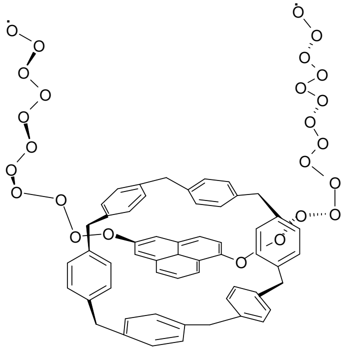


Fig 22 An Anaerobitizer

The suggested structure has an oxygen end that is active because the double bonded oxygen molecule has been converted to a single bonded self propagating oxygen radical with a very reactive end; nothing stops the supramolecules from sucking up the oxygen available to the immediate environment of a human for its self assembly because the reaction has been predetermined by the supramolecules to go on in perpetuity. When this occurs there shall be no free oxygen molecule available to an aerobic organism to rely upon in the immediate environment, thus inadvertently synthesizing an anaerobic world. There are therefore ethical questions in our advancement in scientific research just like the search for anti matter calls for caution, because when we find it, it may consume all of us. It also means that matter the way we know it today could be annihilated and that includes you and I.

It may be proper to point out one of the most important supramolecules known to man. The deoxyribonucleic acid DNA (Fig 23). DNA has two separate strands of nucleotides connected through hydrogen bonds a typical non-covalent form of interaction. This non-covalent bond formation enabled replication to occur in DNA and allow the strands in DNA to be separated and used to template new strands. The result is the fantastic pre-determined double helical naturally occurring **knotane** we named DNA. Our luck is that DNA which pre-determined its arrangement in nature gave us properties that are beneficial to man, and that is sustaining the human idea of the basis of life.

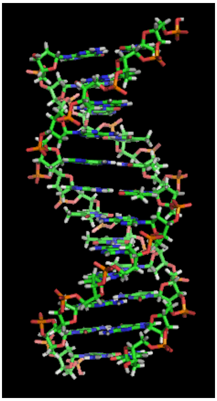


Fig 23 Deoxyribonuclei acid DNA

Subsequently, the forgoing discussion suggests that there may be anti-DNA or negative-DNA. It may not be a DNA molecule with the same number and types of molecules the way known to humans but in its supramolecular arrangement which is pre-determined in a way to act in an exact opposite to DNA by being capable of wiping out life or the basis of life or producing an entirely new generation of supper organisms. The foregoing therefore implores extreme caution in the emerging field of cloning of organisms; because a cloned organism is a giant complex structure that operates among others, on functionalized supramolecular principles intended to exhibit features of life, life latent or even lack of it. We just hope that some evil genius and such supramolecules are not paying attention. Or get some disoriented Chemist or Scientist synthesis or get them templated. The need for ethical involvement in our advanced research in the field of cloning of organisms and search for anti-matter has now become more pertinent. Now that we know that molecules are just waiting for humans to make one silly mistake, trigger them off during any wrong manipulation with molecules, and they would simply say ***thank you*** and take off from there to rain havoc on us. Because from then onwards they can determine both their arrangement and properties, uncontrolled by human and may give the kind of adverse results which only the molecules themselves had predetermined. For instance the explosives known to human were created by humans and they don't explode unless triggered off by human. And when triggered off it is the explosive that determines the outcome of its activity, uncontrolled by human.

6.0 THE PLACE OF NIGERIA IN THE FACE OF ALL THESE CHALLENGES

I have tried upon myself to find out the place of Nigeria in this advancing and changing trend in Chemistry but I am afraid that I could not find because the pace in chemistry has actually kept Nigeria far apart and far behind from the advancing world. We tried to carry out a comparative statistical survey of some university facilities to ascertain our level of preparedness in facing the challenges posed by the latest advancements in Chemistry to see if the reason for our lacking behind was caused by the gods or by ourselves. A histogram plot of the result is shown in Fig 24.

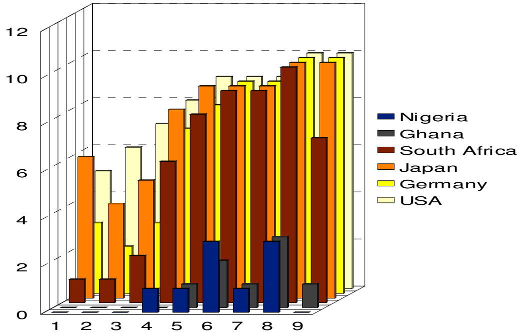


Fig 24 Comparison of availability/preparedness of research equipment for Chemistry in Universities of some countries on a scale of 10

Legend

1 Spectroscopic ellipsometer
2 Electronspray MS
3 Optical microscope
4 GC-MS spectrometer
5 Nuclear Magnetic Resonance spectrometer
6 Ultraviolet-visible spectrometer
7 Infrared spectrometer
8 pH meter
9 Ice making machine

The summary of the result is that while Nigeria (blue) is competing with Ghana (grey) at the lower level of equipment deficiency and lack of simple equipment like ice making machine and pH meter to be out of contention, South Africa (red) is competing with the advanced countries of Japan (orange) and Germany (yellow) at provision of contemporary research equipment like electron and optical microscope to be in contention. In the last world cup however, Ghana left Nigeria behind to be in contention with advanced countries like Germany while South Africa switched gear to join Nigeria in our way out of contention.

Figure 25 is the sort of lab section with simple apparatus that could engage the complexity required by modern day research and concept in our field of ligand metal interactions. This is just a tiny section of one of the six labs showing very simple apparatus (not the sophisticated ones) controlled by this single inorganic chemistry researcher in Europe.

Fig 25 Apparatus on a research bench in a Chemistry lab in Europe

Below in Fig 26 is the equivalence in a Nigerian university showing an entire research bench in a research lab, this time for the entire staff (all area of specialization inclusive) and students of a department. Both pictures have spoken and I need not say more. There is also another problem Mr Vice Chancellor. We are now witnessing the influx of many low quality research students into our labs and that is very worrisome to me for the future of our educational system and the entire country. Many of them don't even want to engage in the research work for which they sort for admission and would gladly pick up an M.Sc or PhD degree without even setting up any experiment or investigation. And serious attempts are now being made by our universities to generate 1st class garbaged 1st class degrees. But that is expected judging from the kind of data and pictures presented above because when garbage is sent in you don't expect any other thing to come out other than garbage. God is there to save all of us but God shall save only those who first and foremost tried to save themselves.

Fig 26 Spaces on a research bench in a Chemistry lab in Nigeria

7.0 CONCLUSION AND RECOMMENDATION

Our research is on a downward trend despite the abundance of very capable hands that we have in the country and we need to take it up again and get it right or face the threats of being swallowed up by the advancing research of the 21st century. It calls for a Research-Academic Revolution on the part of both the lecturers and the poor quality of graduates we are producing. May I recommend the establishment of just one National Instrument Centre that should be mandated to provide any equipment and analytical services for any research area of Chemistry, Physics, Biology, Microbiology and allied disciplines. The one way traffic of having to travel to overseas to conduct any meaningful scientific research is now becoming an eyesore and disgraceful with no end in sight. It brings to question the quality of us as academics before the eyes of our contemporaries overseas whom we visit for experiments that may be as simple as even the determination of melting points of substances.

The National Instrument Centre could be fully funded each year from half of what the papers published were being spent for:

(a) Refurbishing an aircraft runway,
(b) Purchasing cars and refurbishment of houses for our National Assembly members,
(c) Celebration of our Independence day for just one year.

We cannot be asking for veto power and permanent seat in the security council of the United Nations with empty labs and empty stomachs. No Nation gets such privileges with empty labs and empty stomachs.

THANKS FOR LISTENING

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CITATION ON PROFESSOR BIELUONWU AUGUSTUS UZOUKWU

The Vice Chancellor,
Deputy Vice-Chancellors,
Registrar and other Principal Officers,
Provost College of Health Sciences,
Deans of Faculties,
Distinguished Professors and Scholars,
Great Students of Unique UniPort,
Distinguished Guests,
Ladies and Gentlemen.

Professor Bieluonwu Augustus Uzoukwu the University's 73rd Inaugural Lecturer was born in Ajegunle, Lagos on the 19th of August 1957 to Mr Ignatius Ekeyeekwute Uzoukwu and Mrs Agnes Nwaikpeghe Uzoukwu (Nee Nwadike) both from Ozubulu in Ekwusigo Local Government Area of Anambra State. He attended St Theresa's Primary School Apapa Lagos between 1964 to 1966. At the onset of the Nigerian-Biafran hostilities in 1966 he and his parents were forced to relocate to the Eastern Region where he was enrolled into elementary 2 at the St Kevins Catholic Church Primary School Nza Ozubulu in 1966. In 1967 his parents took him to Nnewi to live with his auntie Mrs Ndonnwa Nwafor-Orizu and her husband The Right Honourable Dr A A Nwafor-Orizu, former President of Senate of the Federal Republic of Nigeria and was enrolled into elementary 3 at St Andrews Primary School, Otolo Nnewi. By 1968 when the war was in full swing he was sent back to Ozubulu to live with his parents and was enrolled once again at St Kevins Catholic Church Primary School Nza Ozubulu in elementary 4 where he and his classmates had to attend classes relocated to the shades of the nearby Late Pa Louis

Okoro-Obiajulu's cocoa plantation and plantain trees to escape being easy target for the ever present Nigerian air raids. These classes under the canopy of tall trees went on with occasional relocations here and there until 1969 when he completed his elementary 5. By 1970 when hostilities ended he enrolled into class 1 at Zixton Grammar School Nza Ozubulu where he could not continue after two terms because his parents could not afford the school fees. In 1971 at the request of his auntie he was taken to Nnewi once again to live with his auntie Mrs Ndonnwa Nwafor-Orizu and her husband The Right Honourable Dr A A Nwafor-Orizu who enrolled him into class 1 at the Nigerian Secondary School which later became National Secondary School, Otolo Nnewi. He completed his secondary school education at Nnewi in 1976 with a West African School Certificate obtained at the Division one level. In 1976 the then East Central State Government was offering auxiliary Teaching positions to school leavers who got the West African School Certificate obtained at the Division one or two level. He took the teaching opportunity and was posted to Abbot Girls Secondary School, Ihiala, Anambra State to teach Mathematics in 1976 to class three students.

He was admitted in 1977 to read Chemistry at the University of Ife, now Obafemi Awolowo University, Ile-Ife. In 1979 he benefited from the university scholarship program put in place for Anambra State students by Chief Jim Ifeanyichukwu Nwobodo, the then Governor of the State. He completed his Chemistry degree program in 1981 with a 2nd class honours upper division. During his National Youth Corp Service year of 1982 he was posted to Ijaye High School, Ijaye-Orile, Ibadan where he taught Mathematics and Chemistry to class 3 and 4 students, Physics to class 4 and 5 students and Fine Arts to class 1 and 2 students. On completion of his National Service in 1982 he was employed by the Anambra State Government to teach Mathematics, Chemistry, Physics and Biology to class 3 to 5 students of Basden Memorial Secondary School, Isulo, Orumba LGA. Later he was posted out of Isulo and taught briefly at Girls Secondary School, Aku in Igbo-Etiti LGA and Adada Secondary School, Nkpologu in Uzo-Uwani LGA both in present day Enugu State.

In 1983 he was admitted for a Post-graduate M.Sc program in Chemistry at the University of Nigeria, Nsukka. At the end of the M.Sc examination his supervisor Prof Emmanuel C Okafor recommended based on his examination results that he should proceed straight to a PhD program without completing the M.Sc program that he was originally admitted to read. This recommendation was approved by Senate of the university and by 1988 he was awarded a PhD degree in Chemistry of the University of Nigeria Nsukka. He joined the University of Port Harcourt in 1989 as Lecturer II in the Department of Pure and Industrial Chemistry which he later headed, rose through the ranks as Lecturer I (1992), Senior Lecturer (1995), Reader (2001) and Professor (2006).

Professor Bieluonwu Augustus Uzoukwu main research area is in the area of Analytical- Inorganic Chemistry where he has made immense contribution in the field of ligand metal interaction, coordination chemistry of metal-pyrazolonate species and extraction of metal ions from aqueous solutions contributing over sixty articles in internationally acclaimed journals. Subsequently Professor Uzoukwu has been an Adam Thomson and British Caledonian Airways Scholar to the University of Sussex, United Kingdom; an Alexander von Humboldt Fellow, Germany at three different occasions; an International Foundation for Science Research Scholar and Science Adviser, Sweden at three different occasions. Professor Uzoukwu has presented Lectures on Solvent Extraction of metals to Research Scholars in Poland, Germany, Nigeria and United States of America. He is a member of Chemical Society of Nigeria, Environmental Society of Nigeria, American Public Health Association, Institute of Public Analyst of Nigeria, a Chartered Chemist and Fellow Institute of Chartered Chemists of Nigeria.

On the home front at Ozubulu his home town Professor Uzoukwu is an Ichie and member of the Ozubulu Obi-in-Council and holds the title of Ichie Ideyi-Ozor. He is married to former Miss Ifeoma Nwakaji and they have three children: Soloudo, Ndonwanne and Onwenuzitelu. He is currently the President General of Ozubulu Development Union, but above all a person who believes in God.

Mr Chairman Sir, Principal Officers of the University of Port Harcourt, Professors, Staff and students of the University, invited guests, distinguished Ladies and Gentlemen, it is with great honour and privilege that I introduce this Esteemed Chemist, Renowned Chemical Analyst, a widely consulted Spectroscopist, Academic and Crystallographer; seasoned Intellectual, an Adam Thomson and British Caledonian Airways Scholar, an International Foundation for Science Research Scholar and Adviser, an Alexander von Humboldt Fellow, a Chartered Chemist, an Ichie of the Ozubulu Royal cabinet, a President General and above all a person who believes in God to deliver the 73rd Inaugural Lecture.

APPRECIATION

Alexander von Humboldt Foundation, Germany

International Foundation for Science, Sweden

British Caledonian Airways, United Kingdom

Institut fűr Anorganische Chemie, Technische Universitat Dresden, Germany

University of Port Harcourt

University of Nigeria

The Right Honourable Dr A A Nwafor-Orizu

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