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Peroxo Complexes and Their Oxygen Transfer Reactions

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PEROXO COMPLEXES AND THEIR OXYGEN TRANSFER REACTIONS

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Submitted by

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PREFACE.

The chemistry of the peroxo complexes of various transition metals has received considerable attention in recent years mainly because they are sources of active oxygen atoms and can be used as stoichiometric as well as catalytic oxidants for organic and inorganic substrates; eg., they can be successfully used for the oxidation of olefins, ketones, phosphines, arsines etc. We have successfully employed peroxo complexes to generate glycerine from allyl alcohol which is indeed an industrial aspect of the project.

The present thesis describes isolation and characterisation of different peroxo complexes of Zr (IV), Th (IV), Mo (VI), W (VI) and U (VI) ions containing different bi-dentate, tri-dentate and quardri-dentate ligands. A few oxygen transfer reactions of the complexes towards olefins, ketones, triphenyl phosphine and triphenyl arsine have been investigated.

Some of the work described in the thesis has been published and the remainder is in the process of publication.

1. Some Organoperoxo Complexes of Molybdenum and Tungsten, M.T.H. Tarafder and A.R. Khan, polyhedron, **6**, 275 (1987).
2. Peroxo Complexes of Zr (IV), Th (IV), Mo (VI), and U (VI) ions containing some Bidentate Organic ligands, M.T.H. Tarafder, M.B.H. Howlader, B. Nath, R. Khan and A.A.M. Anowarul Islam, polyhedron, 8, 977 (1989).
3. Peroxo complexes of Zirconium (IV), Thorium (IV), Molybdenum (VI),

Tungsten (VI) and Uranium(VI) ions containing a quardridentate SNNS Schiff Base. M.T.H. Tarafder and A.R. Khan, polyhedron, **10**, 973 (1991).

4. Peroxo complexes of Zirconium (IV), Thorium (IV) Molybdenum (VI), Tungsten (VI) and Uranium (VI) ions containing two quardridentate ONNO Schiff bases, M.T.H. Tarafder and A.R. Khan, polyhedron, **10**, 819 (1991).
5. Peroxo complexes of Molybdenum (VI) and uranium (VI) ions containing two Tetraazamacrocyclic ligands and an organic molecule of high molecular weight, M.T.H. Tarafder and A.R.Khan, Synth. React. Inorg. Met-org. chem. (in press).
6. Peroxo complexes of Molybdenum (VI), Uranium (VI), Zirconium (IV) and Thorium (IV) ions containing some amino acids, M.T.H. Tarafder and A.R.Khan, manuscript submitted to Indian Journal of Chemistry for publication.
7. Peroxo complexes of Zr (IV), Th (IV), Mo (VI), W (VI), and U (VI) ions containing Schiff bases derived from amino acids and salicylaldehyde, M.T.H. Tarafder and A.R. Khan, manuscript submitted to Synth. React. Inorg. Met-org. Chem.(U.S.A.) for publication.

ACKNOWLEDGEMENT.

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Thanks are also due to the Reliance computers for composing the thesis.

DECLARATION

The work embodied in this thesis was carried out by Mr. Abdur Rahim Khan under my supervision and has not been submitted elsewhere for any Degree.

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ABSTRACT

A number of series of peroxo complexes of transition metals containing different organic ligands have been prepared and characterized.

In the first series, peroxo complexes of Mo (VI) and W(VI) ions containing oxoquinolino, aniline-2-carboxylato, 2-aminophenoxido, picolinato, 2-carboxoquinolino and N-(2-oxophenyl) salicylidenimino ligands have been prepared and characterized. These complexes were found to be effective oxidants for allyl alcohol, triphenyl phosphine and triphenyl arsine.

The second series consists of complexes of Zr (IV), Th (IV), Mo (VI) and U (VI) ions containing different bi-dentate ligands viz. phthalic acid, O-phenylene diamine, 2-aminopyridine, 2-aminophenol, ethanolamine, glycol and malonic acid. These complexes were found to oxidize allyl alcohol, triphenyl phosphine and triphenyl arsine.

The third series deals with the complexes of two ONNO Schiff bases formed by the condensation of salicylaldehyde and hydrazine hydrate or O-phenylene-diamine. Metal ions used were Zr (IV), Th (IV), Mo (VI), W (VI) and U (VI). These complexes were found to be inert towards oxidation of olefinic compounds or PPh_3 and $AsPh_3$.

The fourth series of organoperoxo complexes contain a SNNS quardri-dentate Schiff base. The Schiff base was derived from the condensation of S-benzyldithiocarbazate with benzyl. These complexes were also inert towards oxidation.

Two tetraaza macrocyclic ligands 1,4,8,12-tetraazacyclopentadecane ([15]aneN_4) and 5,7,7,12,14,14-hexamethyl-1,4,8,12-tetraazacyclotetradeca-4,11-

diene (trans[14]diene) and an organic molecule of high molecular weight, viz, bis (2,4,4,-trimethyl pentyl) phosphoric acid were used as organic ligands to isolate a few peroxo complexes. The metal ions used were Mo (VI) and U (VI) ions. Complexes of the two macrocyclic ligands were found to be stable towards oxidation and that of the other complexes containing the organic molecule of high molecular weight were found to be active towards oxidation.

The study was also extended to isolate peroxo complexes containing a number of amino acids as ancillary ligands e.g. Glycine, Leucine and Tyrosine. The metal ions used were Mo (VI), U (VI), Zr (IV) and Th (IV). These complexes were found to be effective oxidants for the oxidation of allyl alcohol, PPh_3 and $AsPh_3$.

A few Schiff bases were also derived from the condensation of salicylaldehyde with amino acids, glycine, leucine or phenyl alanine. Peroxo complexes containing these Schiff bases were also isolated. The metal ions were Mo (VI), W (VI), U (VI), Zr (IV) and Th (IV). These were all inert towards oxidation.

The complexes were characterized by elemental analyses, conductivity measurements, IR, NMR and in some cases by mass spectral data. The IR spectra of the complexes indicate that the frequency of the ν_1 mode of the M (O_2) grouping, which is essentially an O-O stretch, decreases with the increase in the atomic number of metals in a particular group.

SYMBOLS AND ABBREVIATIONS

DMF = N, N′ - dimethyl formamide
ATP = adenosine triphosphate
O_2^- = superoxide
O_2^{2-} = peroxide
HMPA = Hexamethyl phosphoric triamide
HOMO = Highest occupied molecular orbital
LUMO =Lowest unoccupied molecular orbital
TPP = triphenyl phosphine
MO = Molecular orbital
[15] ane N_4 = 1, 4, 8, 12 - tetraazacyclopentadecane
DMSO = dimethyl sulphoxide
THF = tetrahydrofuran
IR = infrared spectra
NMR = nuclear magnetic resonance spectra
dipic = 2, 6 - pyridinedicarboxylate
pic = pyridine 2 - carboxylate
TBHP = tert butyl hydroperoxide

CHAPTER 1

GENERAL INTRODUCTION AND LITERATURE SURVEY

1.1: GENERAL INTRODUCTION ON ZIRCONIUM, THORIUM, MOLYBDENUM, TUNGSTEN AND URANIUM METALS.

1.1.1: ZIRCONIUM

Zirconium was discovered by M.H. Klaproth[1], a German chemist near the end of eighteenth century. It is commonly found as silicate, oxide etc. It appears to be nearly as abundant as carbon in the earth's crust. It constitutes nearly 0.017 percent of the earth's lithosphere. The principal ores are baddeleyite, ZrO_2 and Zircon, $ZrSiO_4$. Baddeleyite is found in Brazil and SriLanka and Zircon in New South Wales, India and Brazil. According to H.A. Rowland[2], F.W. Dyson[3] and J.N. Lockyer[4] zirconium occurs in the sun. M. Merrill[5] reported zirconium bands in the spectra of stars and H. Laspeyers[6] in meleorities. Some volcanic lavas contain upto 60% of zirconium.

Zirconium is a bright white metal which is soft, malleable and ductile when pure. It melts at 1875°C. It occurs in three forms (a) crystalline (b) graphitic and (c) amorphous. The crystalline form is hexagonal.

Zirconium and its compounds are used[7] in the arts and industries. Ferrozirconium is used as a scavenger in the steel industry. It is also used in the construction of some wireless valves and in surgery. Zirconia is used in the manufacture of highly refractory[8] crucibles, muffles, resistance cores etc. The use of zirconium compounds-oxide, silicate, carbonate, sulphite and phosphate- as pigments has been patented[9]. The basic acetate is sold as konstrastin for weighting silk[10]. Zircon is used in making the knife edges and planes for balances on account of its hardness. The insolubility of zirconium phosphate in dilute mineral acids makes zirconium nitrate an excellent reagent for removing phosphate ion in qualitative analyses.

1.1.2: THORIUM

Thorium was discovered by J.J. Berzelius[11] in 1815. This was first named Thorine after the god 'Thor' of scandinavian mythology. Thorium is widely distributed in nature, but in very small proportion. J. Joly[12] estimated that the earth's lithosphere contained from $0.2\text{x}10^{-5}$–$3\text{x}10^{-5}$ gm per gm. The thorium minerals are largely concentrated in about five areas. (1) Norway and sweden (2) North America (3) Brazil (4) Urals (5) Tasmania.

J.J. Berzelius[13], the discoverer of this, extracted it from thorite, Th SiO_4. According to C.R. Bohn, most of the thorium compounds in commerce are extracted from monazite, a complex phosphate $(\text{Ce, La, Y, Th})\text{ PO}_4$. Monazite is found largely in Brazil and India.

Soon after the discovery of radioactivity of Uranium, G.C. Schimdt[14] and independently M.S. Curie[15] found that the thorium and its compounds and thorium minerals are also radioactive. Thorium products emit a mixture of α, β and γ- rays. The radio activity of thorium products is a complex effect due to the presence of a series of transformation products derived form thorium itself: Thorium ⟶ Mesothorium-1 ⟶ Mesothorium-2 ⟶

Radiothorium → Thorium -x → Thorium emanation → active deposit of Thorium.

Pure thorium is a soft white metal which is both malleable and ductile and which will burn in the air. Unlike the other metals of the group it is soluble in Hcl. It melts at 1830°C and shows no signs of allotropy.

R. Escales[16] described the use of thorium alloys as reducing agents. E.W. Von Siemens and T.G. Halske [17] recommended an alloy of tungsten and thorium in the manufacture of filaments for incandescent lamps. Thorium is one of the most important raw materials for the production of nuclear energy. Its irradiation in nuclear reactors yields fissionable U^{233} isotope by an (n,γ) reaction. $90th^{232} \xrightarrow{n,\gamma} 90\ Th^{233} \xrightarrow{-\beta^-} 91Pa^{232} \xrightarrow{-\beta^-} 92\ U^{233}$

1.1.3: MOLYBDENUM

In 1782 P.J. Hjelm[18] separated the metal from molybdaena and called it molybdenum. It does not occur in the elemental form in nature. The most important ore of molybdenum is the sulphide, $Mo\ S_2$ which is found as the mineral molybdenite or molybdenum glance; but wulfenite, $PbMoO_4$, is also used as a source of the metal.

Deposits are found in many parts of the world, but chiefly in the United states of America, Mexico, Norway and India. Small amounts of molybdenum (0.1–0.3 ppm) are also widely distributed in fertile soil. The metal which may be a biochemical catalyst, is taken up by some plants, peas and bean containing 3-9 ppm. E. Demarcay[19] observed molybdenum occurring in the ashes of some plants - scotch fir, silver fir, vine, oak, poplar and horn bean. Molybdenum can be extracted both by carbon reduction process and electrolytic process.

Molybdenum is a silver-white metal which melts at 2600°c and boils at 5000°c. It is oxidized in the air at a red heat to molybdic oxide.

The metal is mostly used in the steel industry for making alloys-molybdenum steels and can to a limited extent replace the more expensive tungsten. It volatilizes too easily to be suitable for use as the filaments in incandescent electric lamps, but is used as a filament support both in lamps and in radiovalves. Molybdenite is used as a rectifier in wireless telegraphy. Molybdenum wires has been recommended as resistance wire in electric furnaces[20]. It is used as a substitute for platinum and platinum - iridium alloys[21].

1.1.4. TUNGSTEN

The history of tungsten is closely associated with a mineral which was thought to contain tin, presumably because of its density. Thus J.G. wallerius[22] called the mineral from Bohemia lapids staniferi spathacei. In Sweden, the mineral was called tungsten- from the swedish *tung* heavy or ponderous; and *sten* stone -and A.G. Werner[23] called it schwerstein. The only important ores of tungsten are scheelite $CaWo_4$ and wolframite, (Fe, Mn) Wo_4.

Tungsten does not occur in nature in the elemental form. According to F. clarke and H.S. Washington[24] the average proportion of tungsten in the igneous rocks of the earth's crust is $5x10^{-5}$ percent. The main deposits of tungsten ores are in china, Burma, U.S.A., Bolivia and Portugal; the Chinese deposits being the most plentiful. Tungsten is usually extracted from scheelite. Pure tungsten is ductile and can be drawn out into very fine wire. Its melting point is near 3400°c.

The main use of tungsten is for producing extremely hard and tough steel containing 3-6% of the element. This steel is used for armour plate, projectiles and for cutting tools. Owing to its suitable electrical resistance, high melting point and extremely low vapor pressure, tungsten is now almost the sole metals used for the filaments of incandescent electric lamps.

C. Beindl[25] used it with good results as a catalytic agent in the synthesis of ammonia. Tungsten oxide and Tungestates have been used in dyeing industry.

1.1.5: Uranium

M.H. klaproth[26] in 1786 read a paper : "chemische Unlersuchungen des Uranerze" in which he showed the existence of a new element. He called the element uranium - after the planet Uranus. According to F.W. clarke and H.S Washington[27]. the average proportion of uranium in the igneous rocks of the earth's crust is $8x10^{-5}$ percent. The chief source of uranium is pitchblende, also called uraninite which is a complicated silicate containing U, Pb, Th, Fe, Ca, Bi, Ra, Sb and Zn. The other ores are kasolite, a lead uranyl silicate and carnotite. $K_2O\ 2UO_3 \cdot V_2O_5 \cdot 3H_2O$. The main deposits are in the Belgian Congo and Canada, but there are important deposits in the U.S.A and in Bohemia. In the past, uranium - bearing ores have usually been worked for radium, the uranium being a bye-product. But the possibility of using uranium as a source of nuclear energy has changed this situation and has also made details of improved methods of extraction secret. The radioactivity of uranium was discovered by Henry Becquerel[27] in 1896. Uranium and its compounds are largely used as a source of nuclear energy eg for the preparation of hydrogen bombs. Other uses of uranium are in the manufacture of iron alloys[28] in photometry[29] as a dye for textile leather and wood[30] in medicine for diabetes[31] etc. It is also used as a catalyst in chemical processes[32] and x-ray anticathodes. Four countries Canada, south Africa, U.S.A and France control 85 to 90 percent of the world's known low cost uranium reserves.

1.2: OXYGENATED COMPLEXES OF TRANSITION METALS
(peroxides, superoxides and μ-peroxides)

Dioxygen, superoxo and peroxo complexes of transition metal centres have received wide spread attention[33-43] owing to the relevance of this chemistry to oxygen transport and catalytic activation as in the biological O_2 carriers, oxygenases, peroxidases and hydroxylases[44]. Metal peroxides are key compounds in this area and we have a programme in our laboratory to synthesize new organoperoxo complexes of different transition metals of group 4A and 6A in order to gain a deeper understanding of the factors which influence the reactivity, structure and bonding in these novel compounds.

Dioxygen itself is a reactive entity but since it has a triplet ground state, its direct combination with organic molecules is a spin-forbidden process[42]. Tranistion metals having multiple spin and oxidation states can readily interact with dioxygen, and in some cases, they form isolable oxygen adducts. In these associations the metal acts as a reducing agent by filling the antibonding π_g^* orbitals of dioxygen. It increases the O–O distance and facilitates its cleavage. The oxygen molecule is thereby activated and the chemist may take use of this activated oxygen for scientifically or technologically interesting oxidation reactions.

Investigation into the fixation and activation of molecular oxygen by transition metals were largely initiated because of an interest in model compounds that are used in studying reversible oxygenation mechanisms involved in the very complex natural oxygen carriers eg the hemoglobins and hemocyanins;

Viz,

$MLi + O_2 = O_2MLi$;

M = Fe ; Li = porphyrin ligand.

The respiratory pigments are able to fix oxygen molecules from the atmosphere, to transport them to their sites of reaction and there to release them. This is in a sense, is a catalytic process and is reversible. The respiratory chain used to produce energy in the form of ATP (adenosine triphosphate) in aerobic metabolism is based on the reductions of oxygen to water and is extremely efficient.

A common feature of these reactions is the involvement of metal atoms in complexing and activating oxygen.

The dioxygen-metal adduct Mo_2, can have either the " Superoxo" structure (O_2^-) when the metal is a potential one-electron donor or the peroxo structure (O_2^{2}) when the metal is a potential two-electron donor. These dioxygen adducts may further react with a second metal to produce the "μ-peroxo" species MO_2M, which can be transformed either by cleavage of the O-O bond into the "OXO" species M=O or by loss of one oxygen atom into the "μ- oxo" specie M-O-M. The hydroxo species M-OH can be further obtained by hydrolysis of the Oxo complex. The oxygenated complex of transition metals are shown in Fig 1.

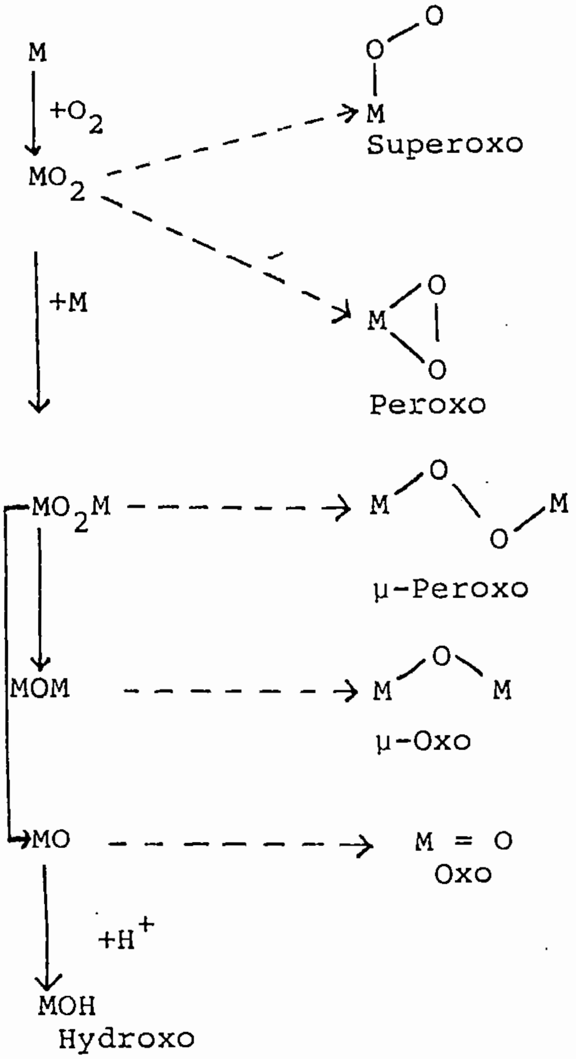


Fig. 1. Oxygenated complexes of transitional metals.

All these six different types of oxygenated complexes can be considered as potential sources of oxygen atom liable to be given to reactive substrates.[42,45] .

(i) Superoxo complexes are the primary reversible dioxygen adducts occurring naturally in the oxygen-carrying iron-porphyrin respiratory pigments such as myoglobin. They also intervene as precusors of active peroxidic species in enzymatic monooxygenases containing the cytochrome P_{450} as prosthetic group[42].

(ii) Peroxo and μ - peroxo complexes containing dioxygen are bonded to the metal in a peroxidic form. They are responsible for various selective oxidations such as epoxidation, Ketonization, oxidative cleavage of olefins and Bayer-Williger lactonization of Ketones etc.

(iii) μ - oxo complexes have been shown to be the active species in copper catalyzed oxidation of alcohols to Ketones and oxidative cleavage of pyrocatechol[42].

(iv) Oxo complexes often behave as carbenic reagents and are responsible for various oxidation reactions, eg, epoxidation of olefins, oxidative cleavage etc.

(v) Hydroxo complexes intervene in Wacker - type oxidations involving hydroxy-palladation of olefins giving carbonyl compounds.

We are interested only for the reactivities of the peroxo complexes.

1.3: THE BONDING OF OXYGEN TO METAL

1.3.1: The electronic structure of dioxygen compounds :

The bonding in molecular oxygen is best described by molecular orbital theory[46]. According to this theory the valence orbitals of the two oxygen atoms ($2S^2 2P^4$) combine to give molecular orbitals whose relative energies are shown in Fig 2.

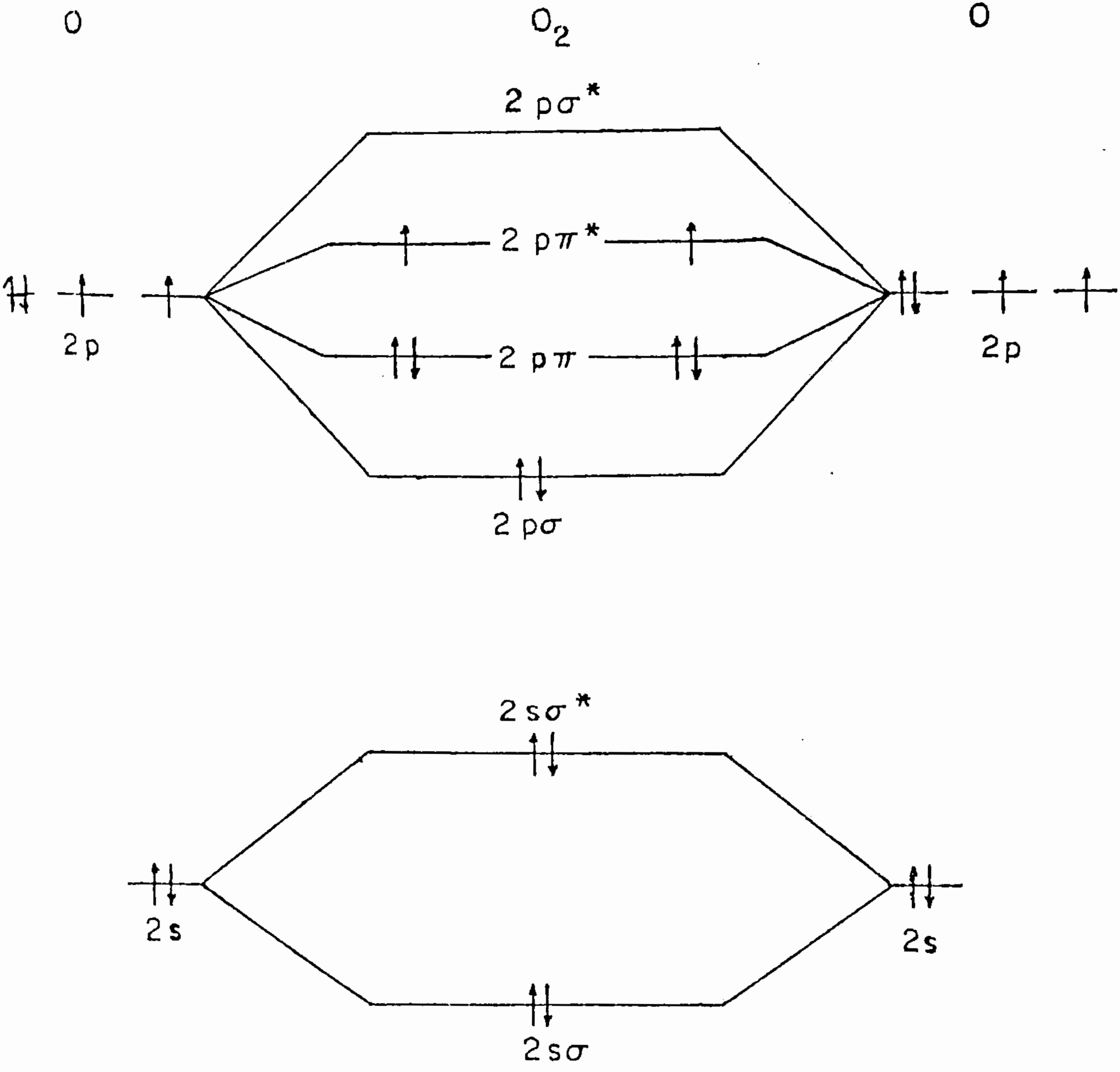


Fig. 2. Molecular orbital diagram for O_2.

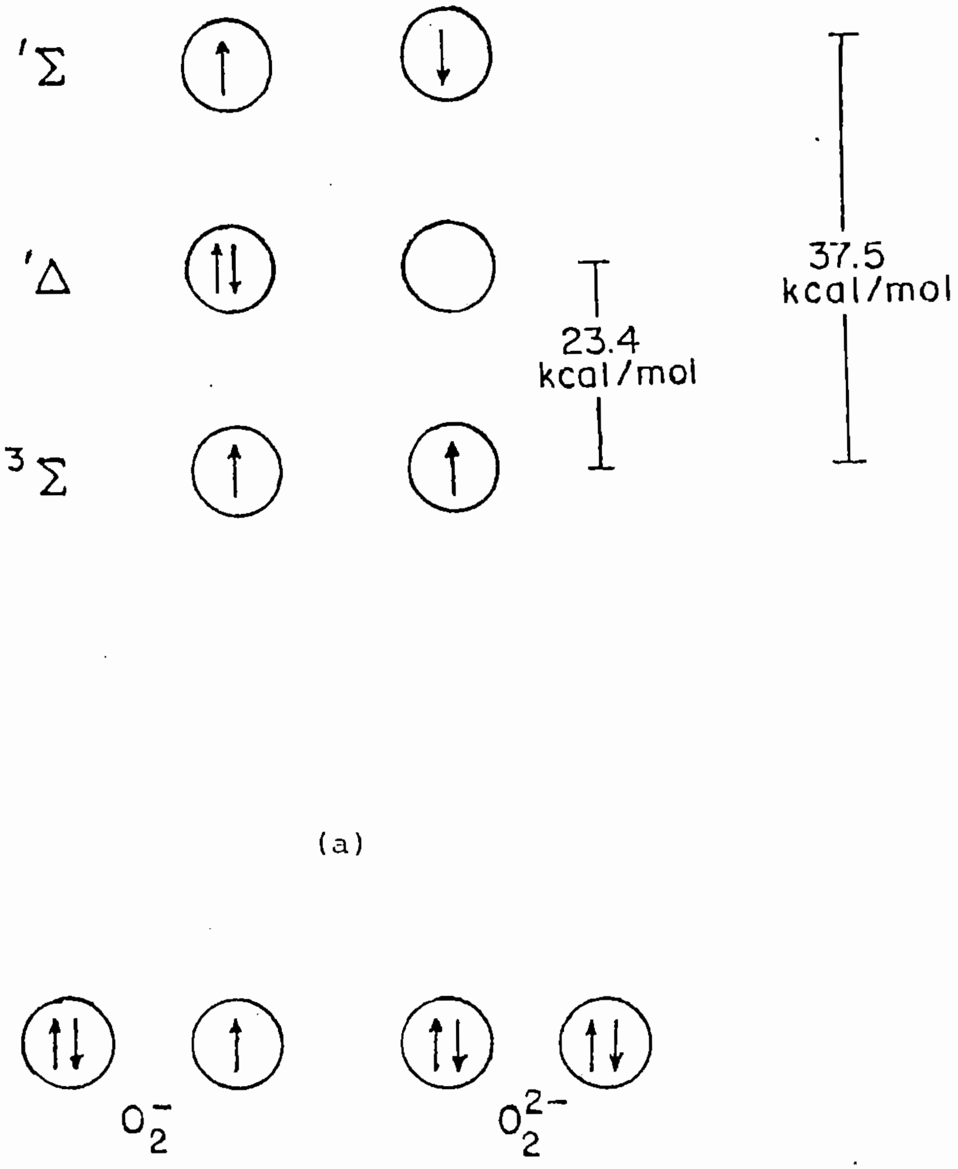


Fig. 3. (a) π^* orbital occupancy and energies of the first two electronically excited states of O_2.

(b) π^* occupancy of superoxide and peroxide.

The ground state of molecular oxygen is observed to be a triplet state (3_{g}) with two unpaired electrons occupying a pair of degenerate π^* antibonding orbitals. The two lowest excited states are formed by redistributing the two electrons in the 2P π^* orbitals. The configurations and energies for the ground states and first two excited states are shown in Fig 3.

Molecular orbital theory also predicts bond orders of 2.5, 2. 1.5 and 1 for the dioxygenyl cation O_2^+, molecular O_2, superoxide O_2^- and peroxide O_2^{2-} respectively.

The molecular orbital diagram given in Fig 2 is valid for a free oxygen molecule but for O_2 under the influence of the electrostatic field of a transition metal ion in a complex, the situation will be some what different. It was first postulated by Griffith[47] that this influence might remove the degeneracy of the $2P\pi^*$ level and that in certain cases, the energy difference between the two orbitals may become larger than the energy of pairing i.e. the two electrons will then be located in the more stabilized of the two orbitals with their spin paired (Fig 4).

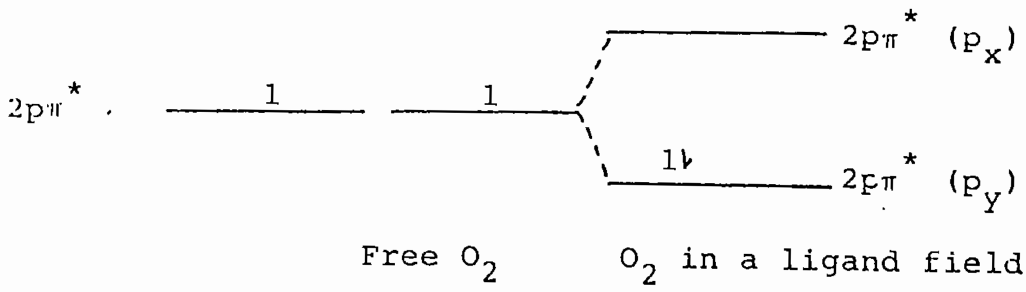


Fig. 4. Influence of a ligand field on the electron distribution in the oxygen molecule.

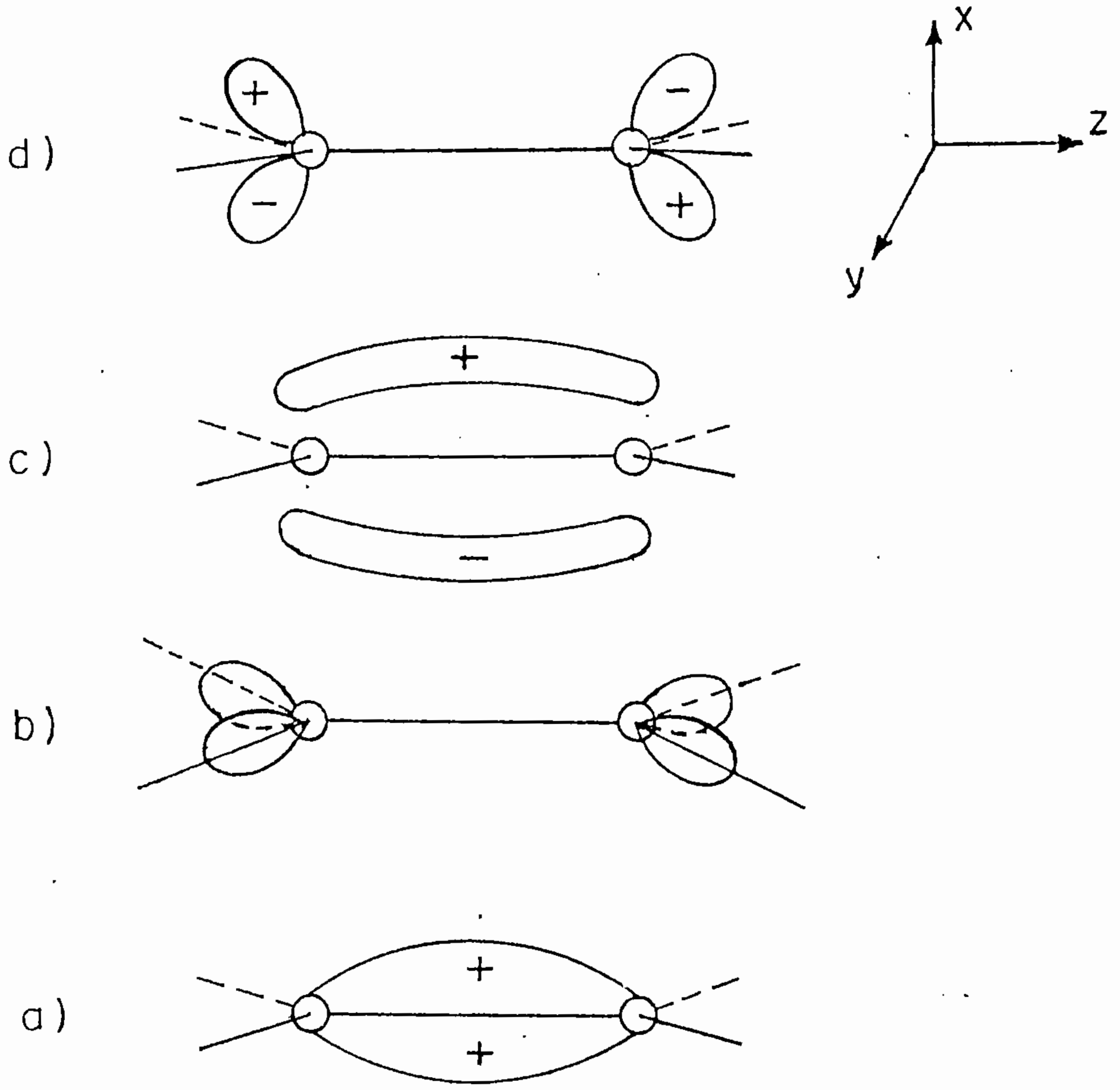
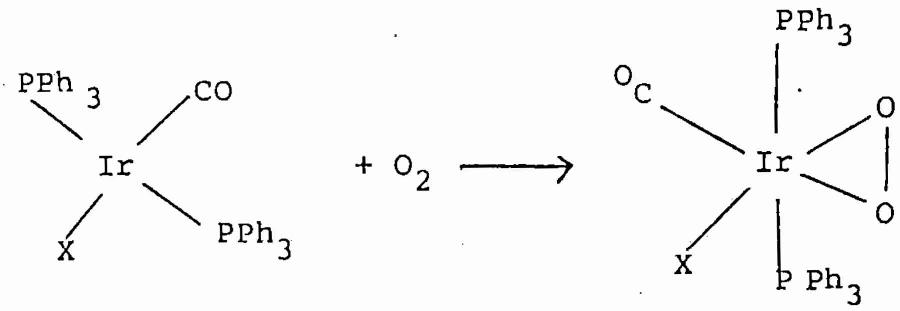


Fig. 5. The "valence state" molecular orbitals of the oxygen molecule: a) σ-bonding MO; b) sp^2 lone pair orbitals (n_O); c) π-bonding MO; d) π^*-antibonding MO (according to (38)).



[2]

Fig. 6. Vaska's peroxo complex.

Fig. 7. Diagrammatic representation of the possible modes of O_2 binding to metal ions.

Griffith has also indicated that in this situation the oxygen molecule has an electronic configuration comparable with that of ethylene in its ground state. We may therefore, visualize the electron distribution in terms. of a trigonal Sp^2 hybridization at the two oxygen atoms. One of the sp^2 hybrid orbitals of each oxygen atom is used for mutual σ- bonding and the other two are each doubly occupied ; in other words, they form a set of four lone pair orbitals (n_0) oriented in the same way as the four hydrogen atoms in ethylene (Fig 5). There is also one effective π- bond in the molecule ; the lowest energy empty antibonding orbital is $2P\pi^*$ (Px)

1.3.2: Bonding in metal dioxygen complex.

Two basic classes of metal dioxygen complexes have been proposed as model systems; those incorporating dioxygen in a side-on linkage (the vaska-type complexes Fig. 6)[47-49] and those involving a single metal dioxygen σ-bond, proposed by pauling and others (Fig. 7) [50-52]. The former class, discovered and intensively studied by vaska [34,53] and others [39,41-43,54-57] were said to have covalent linkages between the metal and the peroxide group in an isosceles triangular fashion. Perhaps the simplest way to understand the metal peroxide interaction would be through the comparison of O_2^{2-} and C_2H_4 as ligands[48]. In the ethylene complexes, the olefin is usually considered as donating electrons from the π bonding orbital to the metal, while the metal donates electrons from an appropriate filled d orbital to the empty, antibonding π^* orbital of the olefin. In the peroxide ion, the π^* orbital is already filled, so that no back bonding is possible. At the same time, there may be donation to the metal both from the π- and π^* orbitals of the peroxide group, at least when the metal is in a sufficiently high oxidation state. The effect of coordination on the O-O bond would then depend on the relative strengths of the two interactions - in other words, on whether donation was principally from π - or from π^* orbitals of the peroxide group (Fig 8).

It has been mentioned that removal and addition of electrons to the π^* orbital of dioxygen brings about many changes as summarized in Table 1[34,58].

Table 1. Properties of dioxygen and its ions.

	Bond Order	O-O A°	Bond Energy kcal mol^{-1}	ν(O-O) cm^{-1}
O_2^+	2.5	1.12		1905
↑				
O_2	2	1.21	118	1580
↓				
O_2^- (Superoxide)	1.5	1.33		1097
↓				
O_2^{2-} (Peroxide)	1.0	1.49	35	802
↓				
$2O^{2-}$	0			

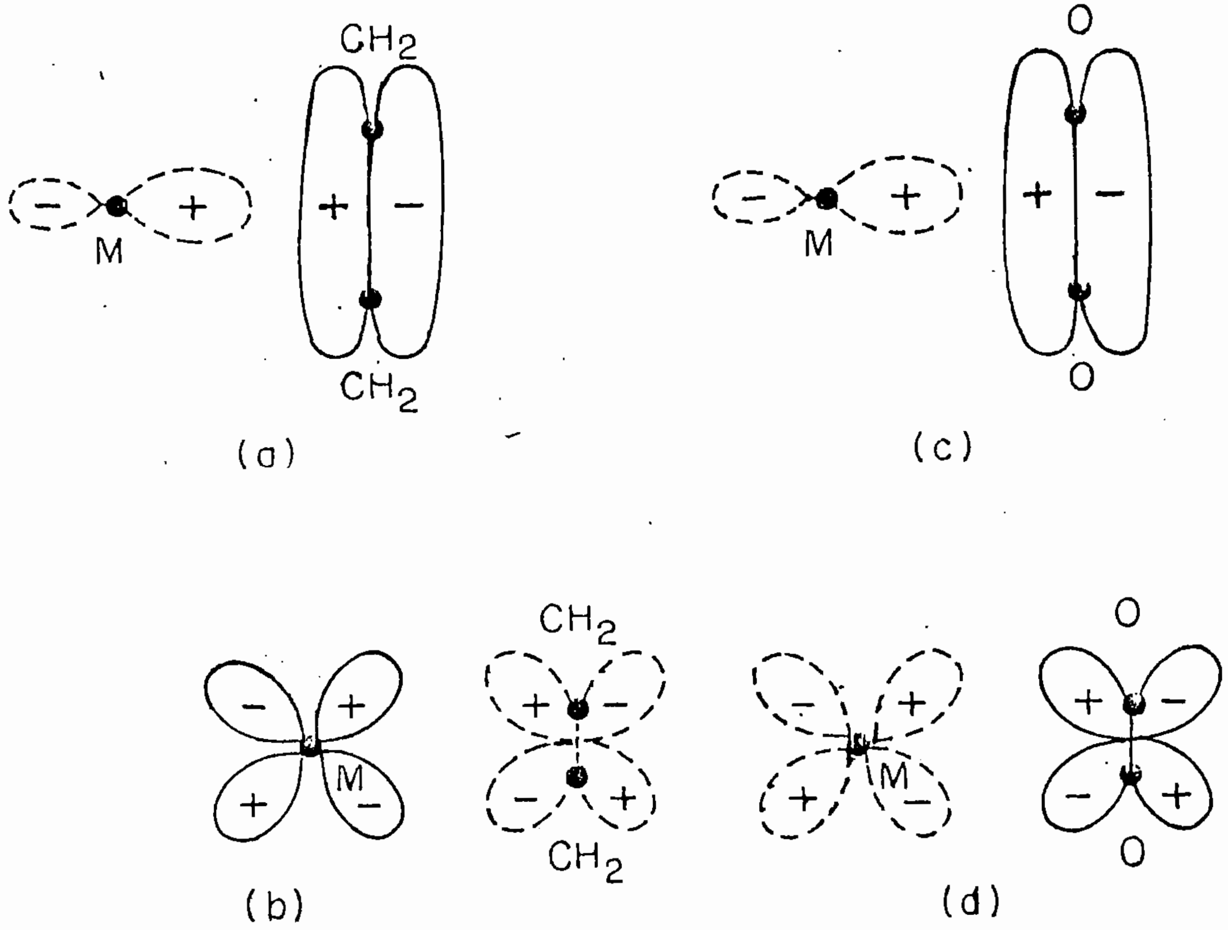


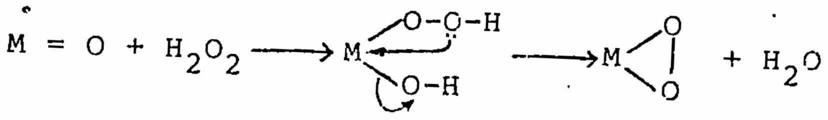
Fig. 8. Possible scheme for representing the interaction between a transition metal atom and ethylene or peroxide as ligands. (a) Donation to the metal from a π-bonding orbital of ethylene; (b) donation from the metal to a π-antibonding orbital of ethylene; (c) donation to the metal from a π-bonding orbital of peroxide; (d) donation to the metal from a π-antibonding orbital of peroxide. An orbital indicated by full lines contains an electron-pair; those indicated by broken lines are empty. For simplicity, the metal orbital interacting with the π-bonding ligand orbitals have been drawn as sp hybrids, although they will probably have d-character[48]

1.4: MODE OF FORMATION OF TRANSITION METAL PEROXIDES.

The dioxygen complexes which are referred to as the side- bonded or π - bonded dioxygen complexes are diamagnetic and can be obtained by two principal methods[41,42,57,59].

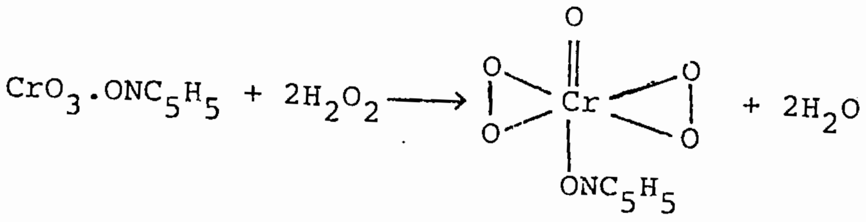
1.4.1: Ligand exchange by reaction of O_2^{2-} and a high-valent metal complex; an acid-base interaction :

Specifically, this consists of reaction of hydrogen peroxide with a complex containing a metal in a higher oxidation state.

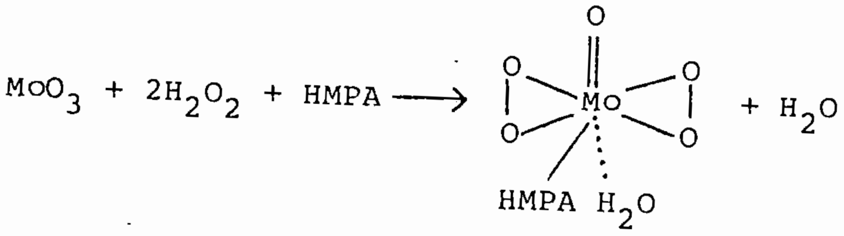


[3]

Examples:



[4]



[5]

or

[6]

In these examples, the dioxygen is provided in an already reduced (peroxide) state. The metals in their higher oxidation states do not enter into back bonding to dioxygen. Complexation occurs from the (Lewis) acid-base interaction between the metal ion and the peroxide ion.

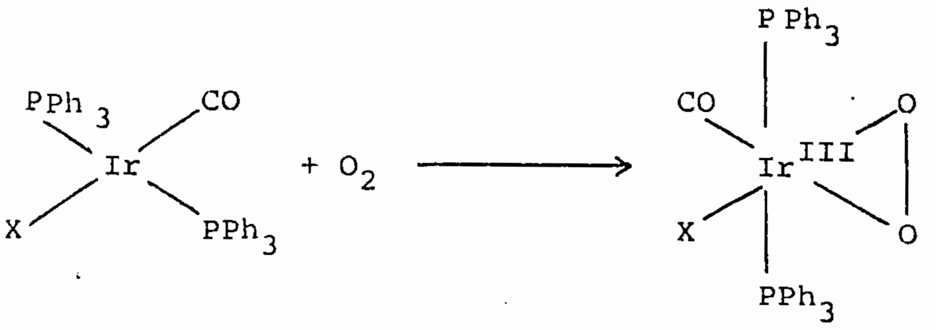
A great number of peroxo complexes of group 4A, 5A and 6A have been prepared by this method and shown by X-ray crystallographic structure determination to exhibit the triangular model of bonding of peroxide to metal[39,48,54,57,61]. For most of these complexes, there is very little variation in the O-O bond distance despite differences in the metal, ancillary ligands, valence state and structure[42].

1.4.2: Oxidative addition of dioxygen to a complex of a low valent metal.

The second method of obtaining peroxo complexes is the direct introduction of dioxygen with reduced, two electron donor metal complexes. The peroxidic nature of dioxygen adducts such as M $(PPh_3)_2O_2$ [M = Pd, Pt] has been demonstrated by obtaining hydrogen peroxide upon hydrolysis of the complexes with strong acid[60].

[7]

Examples:



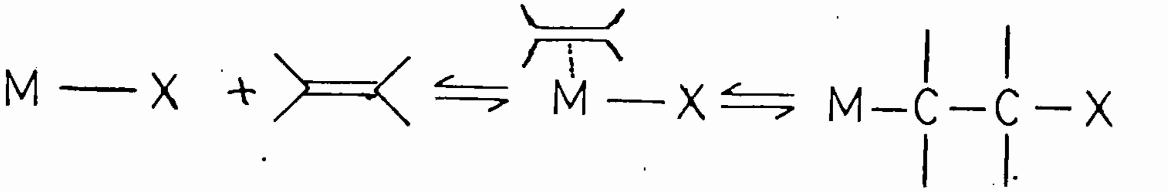
[2]

[8]

1.5. TRANSFER OF COORDINATED OXYGEN FROM TRANSITION METAL PEROXIDE TO ORGANIC SUBSTRATE.

The peroxo complexes can be considered as potential donors of oxygen to reactive substrates. The primary oxygen source for the preparation of these peroxidic complexes can be either molecular oxygen itself or peroxidic compounds such as hydrogen peroxides or alkylhydroperoxide. Hence the way in which transition metal peroxides release oxygen to substrates is particularly relevant to the catalytic properties of transition metal complexes in selective oxidations involving O_2, ROOH or H_2O_2 as the oxygen source.

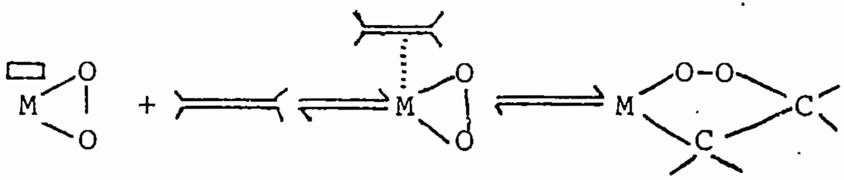
In order to understand better the reactions of peroxo complexes, it is instructive to consider the general reaction of olefin with M-X group. The key step in most of the transition metal catalyzed transformations of olefins consists of the π-σ rearrangement of the olefin on the metal shown by the equation (9).



[9]

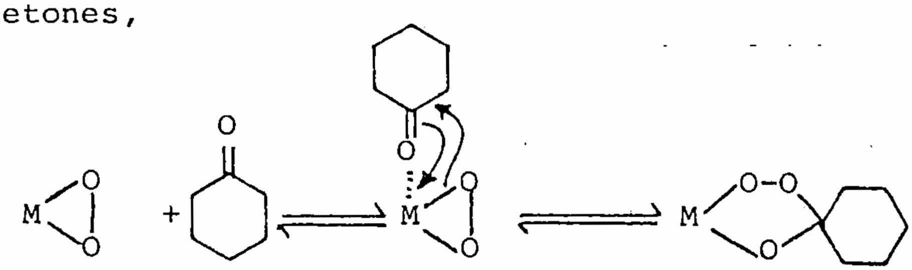
This transformation can be described as the insertion of the coordinated olefin into metal - nucleophilic bond M-X. In the case of metal bearing oxygen atoms, the application of this general principle leads to a peroximetallation process if the metal is bonded to a peroxidic group, or to an oxymetallation process if the metal is bonded to an oxygen atom as in oxo or hydroxo complexes.

The insertion of substrates such as olefin or ketones into the metal peroxides give rise to the formation of a five-membered peroxymetallocyclic adduct e.g. for olefins.



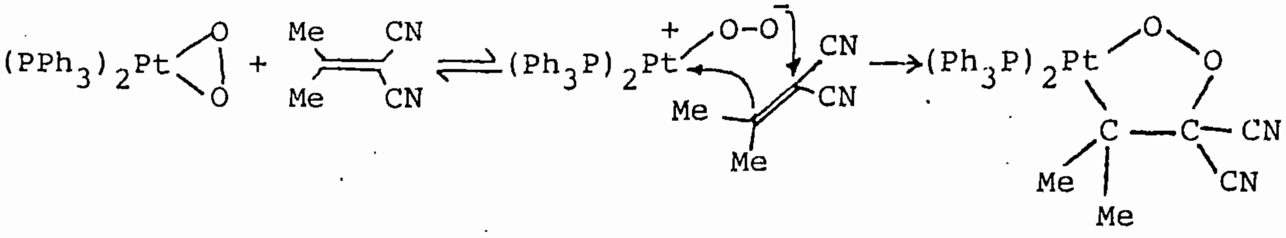
[10]

For ketones,

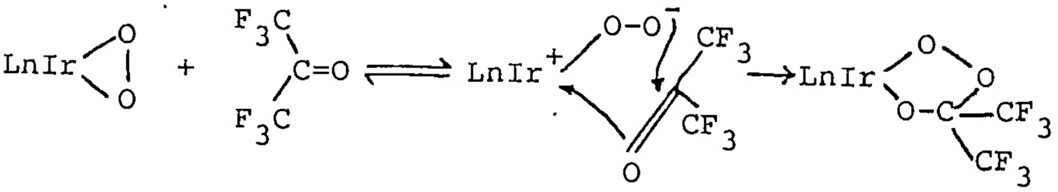


[11]

The coordination of the substrate to the metal prior to insertion is only necessary for nucleophilic substrates[42,63]. For electrophilic substrates such as cyano olefins or hexafluoro acetone, this preliminary coordination is not necessary and the peroxo metallocyclic adduct results from the bimolecular 1,3- dipolar addition of the substrates to the peroxo group as shown in equations [12][64] and [13][65]



[12]



[13]

1.6: AIM OF THE PRESENT WORK.

Studies on the peroxo complexes have received considerable attention in recent years because many of these complexes are efficient stoichiometric and catalytic oxidants for organic and inorganic substrates. The reactivity of metal peroxides can be greatly modified by introducing metals of different sizes and ancillary ligands with different donor properties. In particular peroxo complexes containing lighter metals for instance [$Zr(C_5H_5NCOO)_2(O_2)$] were kinetically stable towards olefinic compounds whereas the analogous complexes of heavier metal, like, thorium was an efficient oxidant. It was therefore, an interest to synthesize new peroxo complexes of the lighter transition elements, viz, zirconium and molybdenum and also some heavier transition elements, tungsten, thorium and uranium. It was aimed to isolate peroxo complexes of the above metals containing mono-dentate, bi-dentate, tri-dentate and quardridendate organic ligands. It was also of interest to isolate peroxo complexes containing tetraaza-macrocyclic ligands, amino acids and compounds of high molecular weights, viz., Lix-34c cyanex-272, Lix-54 etc. Investigation into the reactivity of these complexes towards various substrates was also a subject of our interest. A comparative study dealing with the stabilities of the peroxo complexes based on the size of the metal as well as on the nature of coligands used will also be the subject of our interest.

1.7: LITERATURE SURVEY

Oxygen carrier complexes have many uses. One of the novel application was their use by the U.S Navy during world war II to supply oxygen for welding and cutting purposes[66-67].

Dioxygen complexes of transition metals besides having an intrinsic interest of their own are of considerable and growing importance for their ability to catalyze oxygen insertion reactions and oxidation of organic substrates.[33,34, 40-43,48,54,55,58,68-73]

In this respect, they may be compared in some ways to "oxygenases" and "oxidases" respectively.

A great number of transition metal complexes with oxygen as a ligand are known. As early as 1852 Fremy[74] reported that " ammonia-cobalt salts" and particularly the nitrate, absorb oxygen from the air and release it again when dissolved in water.

In 1933 pfeiffer *et al.*[75] reported that the red brown crystals of bis-salicylaldehyde-ethylene diimine cobalt (II) complexes darkened on exposure to air. Tsumki[76] proved that the colour change was due to reversible sorption of molecular oxygen but it was a long way from there to the more sophisticated cobalt (II) chelates, which are considered now as suitable model substances for the natural oxygen carrier systems and to the catalytically active transition metal-oxygen complexes. These have been extensively reviewed[58,66,68,73,77,78]

Oxygen transfer from peroxo complexes to substrates:-

Chromium, molybdenum and tungsten oxodiperoxo complexes with the general formula $M(O)(O_2)_2L_2$ have been obtained by reaction of a ligand, L (eg. amide, phosphoramide, amine, phosphine oxide, arsine oxide, aromatic amines and their oxides) with a solution of MoO_3 or WO_3 in hydrogen peroxide[41,79].

These complexes, which are soluble in organic solvents, are able to react with various reactive substrates. Mimoun *et al.*[33,42] have studied epoxidation of olefins by $[Mo(O)\ (O_2)_2\ HMPA.\ H_2O]$ and showed that the reaction proceeds via two steps: reversible coordination of olefin to the metal displacing the ligand, followed by irreversible oxygen transfer to the olefin.

Displacement of the ligand L by the olefin has been shown to occur using NMR measurements and kinetic studies. Further, a strong inhibitory effect of the presence of σ donor ligands on the rate of epoxidation has been observed[42].

Since coordination of olefin to the metal is the rate determining step, epoxidation occurs more readily when the olefin possesses substituents which make it more nucleophilic[42].

Several mono peroxo-molybdenum complexes, $[Mo(O)(O_2)Ln]$[80] and dideroxo-molybdenum complexes, $[Mo(O)(O_2)_2\ L_1L_2]$[81] have been prepared and found to epoxidize many different types of alkenes[82].

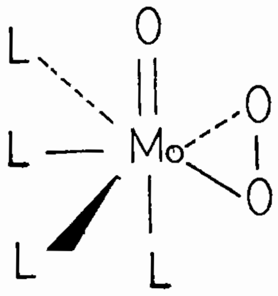


Fig. 9: monoperoxo molybdenum complex

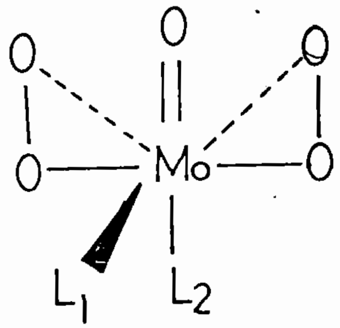


Fig. 10; diperoxo molybdenum complex

Among the monoperoxo-molybdenum complexes synthesized are $Mo(O)(O_2)$(dipic) H_2O, $Mo(O)(O_2)$ $[PhCON(ph)O]_2$, Mo $(O)(O_2)X_2L_2$, $Mo(O)(O_2)$ Cl (pic) and $Mo(O)(O_2)$ Cl_2. HMPA epoxidises unactivated alkenes, but the epoxide is mainly formed at the beginning of the reaction and progressively disappears to be replaced by products of oxidative cleavage[85].

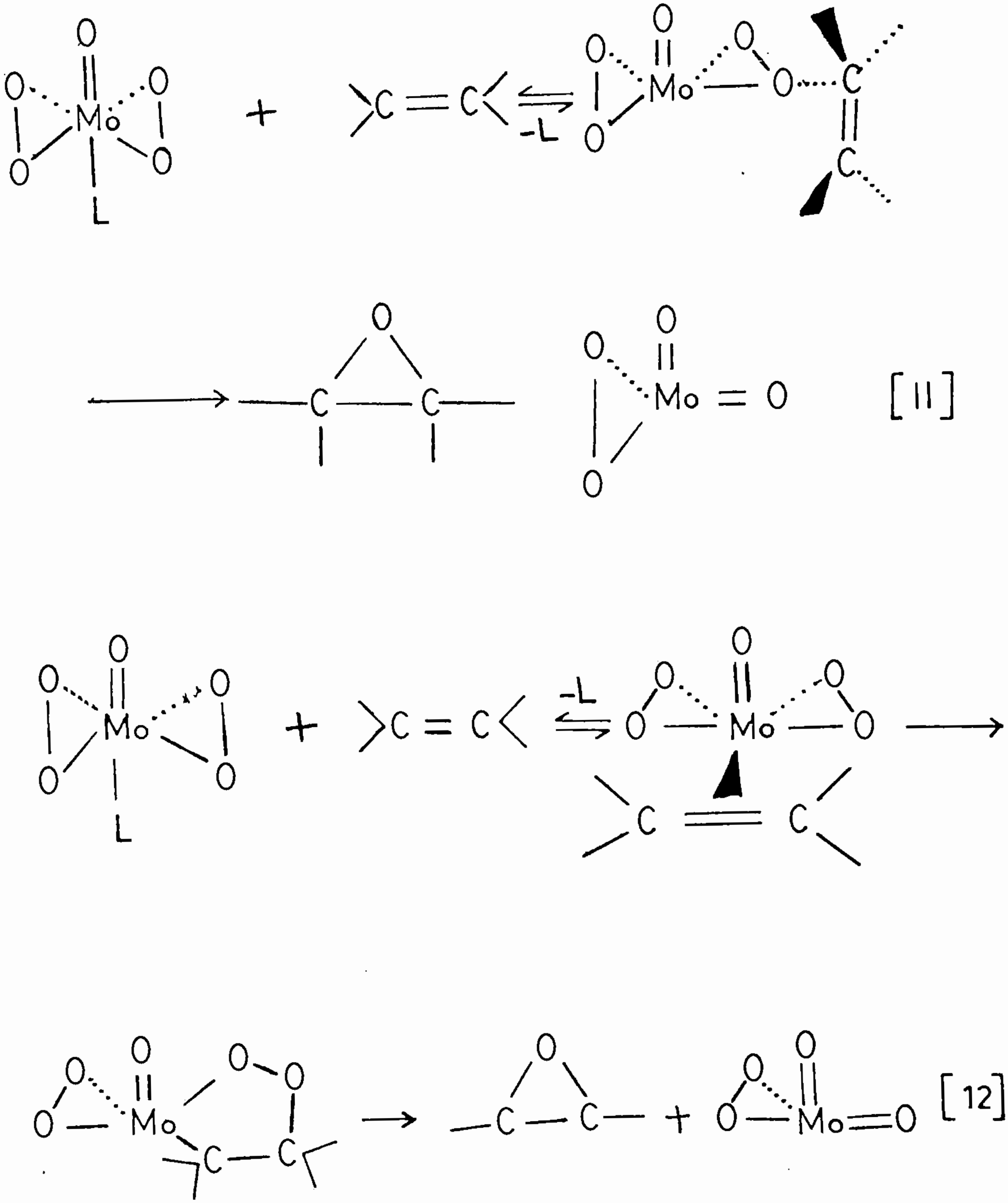
The diperoxo-molybdenum complexes (fig 10) can be easily prepared from addition of the ligands to a solution of MoO_3 in hydrogen peroxide[86].

The diperoxo molybdenum complexes have been found to stoichiometrically oxidize alkenes to epoxides in good yields at room temperature in aprotic solvents[33,38,86-90].

The epoxidation of alkenes is stereo selective, ie cis-alkenes are transformed into cis-epoxides and trans-alkenes into trans-epoxides[38,82].

The mechanism for the transfer of an oxygen atom from Fig 10 to an alkene has been the subject of many discussions. Spectroscopic and kinetic studies reveal that the first step in the epoxidation of an alkene by $Mo(O)(O_2)_2$. HMPA is a reversible displacement of the ligand (probably the equatorial) by the alkene, followed by irreversible oxygen transfer to the alkene[33,88,91]. It has been observed that the rate of epoxidation is reduced by the presence of σ-donor ligands, and furthermore, complexes with equatorial positions adjacent to the peroxo moiety occupied by anionic ligands or strongly complexing bidentate or tridentate ligands are unreactive[42]. ^{18}O-Labeling studies demonstrate that it is the peroxygen that is transferred to the alkene[34]. The reactivity of the alkenes increases with their nueleophlicity[33]. The two mechanisms suggested for the oxygen transfer from $Mo(O)(O_2)_2$ to an alkene are outlined in scheme 1.

The first mechanism (scheme 1 [II] involves interaction of the alkene with one of the peroxygens; this mechanism is similar to those suggested from both an experimental and a theoretical point of view for epoxidation with group IV and V transition metals and peroxides as well as epoxidation of alkenes with per-acids. The second mechanism, (scheme 1 [12] starts with the coordination of the alkene to molybdenum by which the alkene loses its nueleophilic character, II. The next step consists then of an intramolecular 1,3 dipolar cycloaddition of the peroxo group to the coordinated electrophilic alkene, yielding a five membered peroxometallocycle, 12, which decomposes by a 1,3-dipolar cycloreversion mechanism to the epoxide and the $Mo(O)_2(O_2)$ complex.



SCHEME 1

The two HOMOs of 10 are mainly of pz and px character at the peroxygens and antibonding, schematically shown in 13 and 14 whereas among the LUMOs an orbital with py character, σ antibonding between the two peroxygens is found in 15[92].

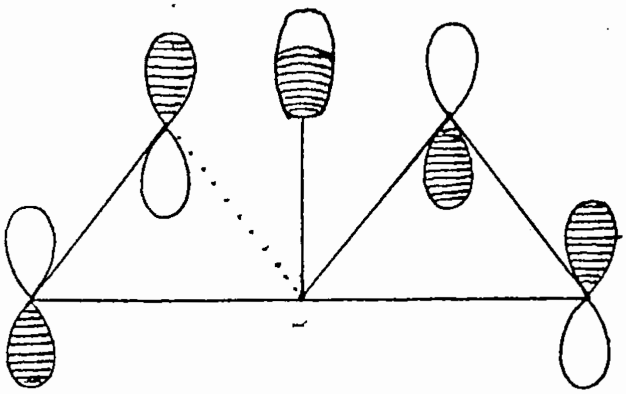
The empty orbitals of 10 are mainly d orbitals at molybdenum and thus able to interact with ligands.

The two mechanisms in scheme 2 for the epoxidation of alkenes have been suggested on the basis of frontier orbitals of $Mo(O)(O_2)_2$[92].

The first step in the two mechanisms is the coordination of the alkene to molybdenum in a parallel (scheme 2, route a) or perpendicular (scheme 2, route b) orientation relative to the molybdenum-peroxo plane. By a slipping motion of the alkene from the two orientations at the molybdenum atom toward one of the peroxygens favorable interactions between the π and π^* orbitals of the alkene and 15 and 14 (or 13) become possible. The similarities of the transition state 16 and 17 and of those discussed in relation to oxygen transfer from the other d^* transition metal alkylperoxo complexes outlined above are thus obvious. It was not possible on the basis of the extended- Huckel calculations to distinguish energetically between 15 and 16. The total energy for 12 was found to be higher than those of the transition states in the mechanisms in scheme 2[92].

Olah *et al.*[40] carried out the epoxidation of many organic olefinic compounds with uranyl peroxide, $U(O)_2(O_2)$. $4H_2O$. They also proposed a mechanistic path for epoxide formation similar to Mimoun's.

Jacobson *et al.*[39] have reported oxo di- and mono-peroxo complexes of Mo and W containing picolinato and pyridine-2,6-dicarbxylato ligands of



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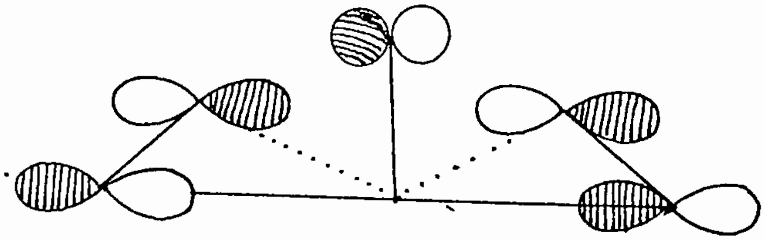

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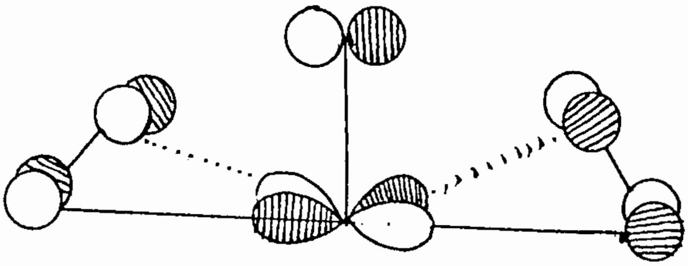

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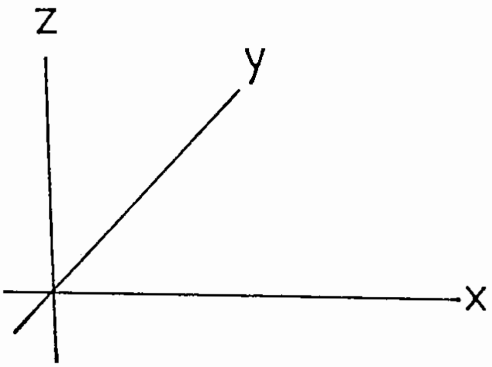
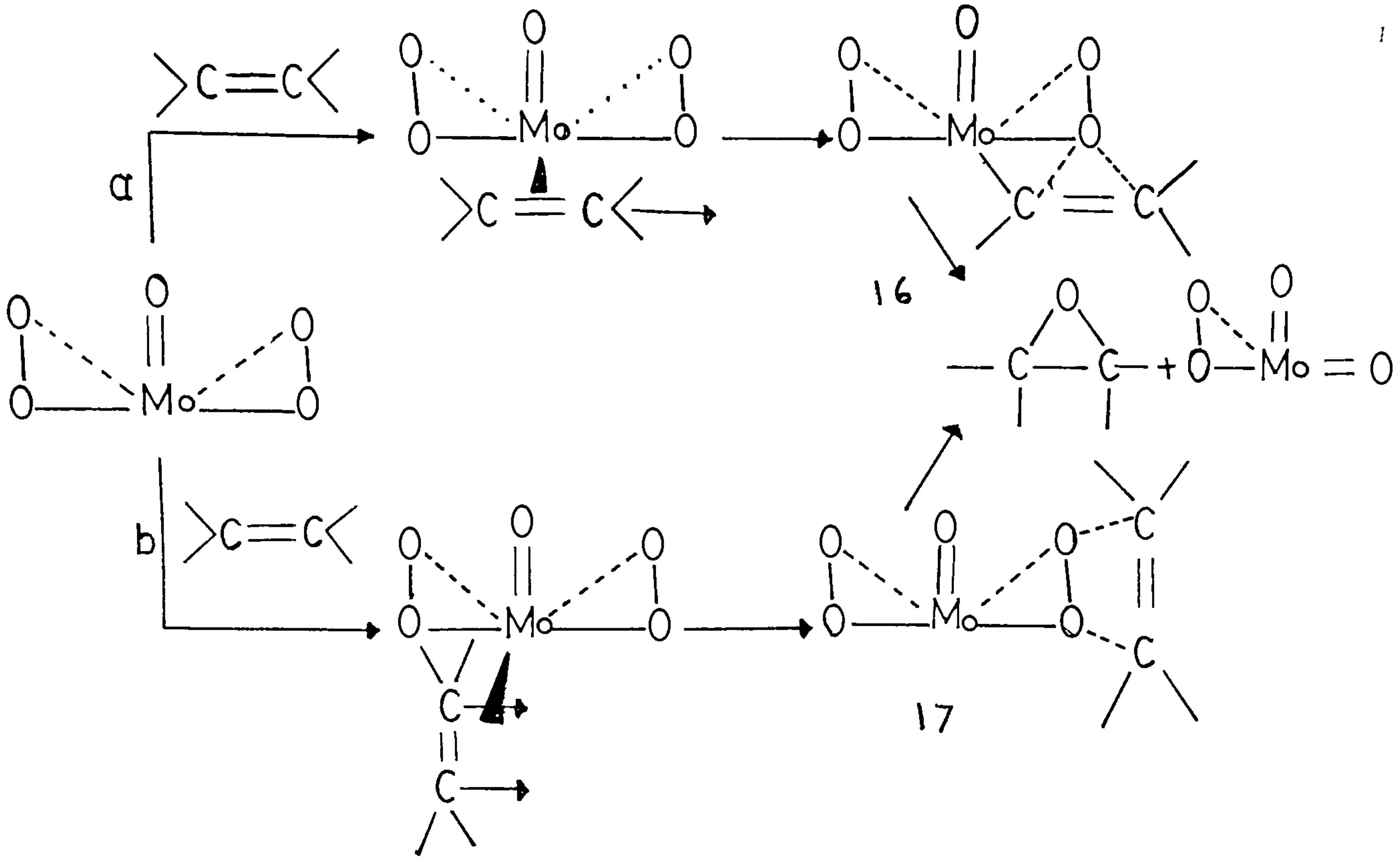
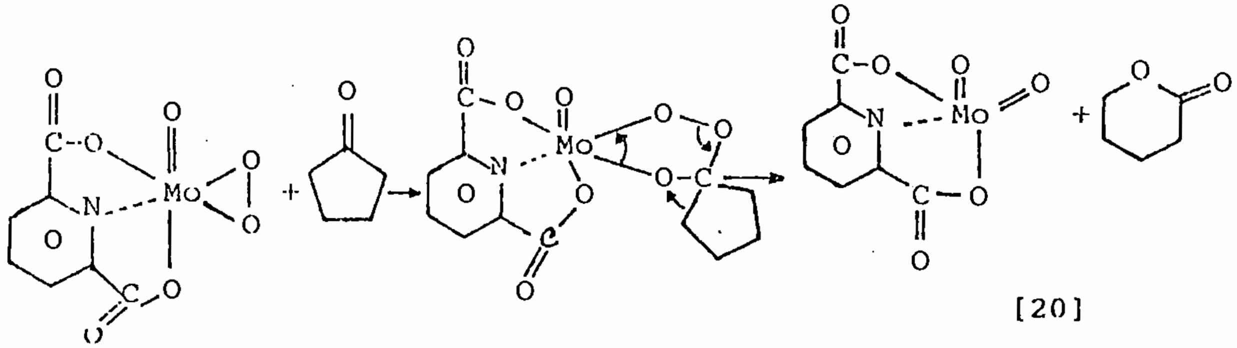




SCHEME 2

general formulae $[M(O)(O_2)_2\ C_5H_4NCOO]^- H_3O^+$ and $[M(O)(O_2)\ C_5H_3N(COO)_2]H_2O$. They also reported characterization of peroxo complexes of Mo and W having outer sphere uncoordinated ligand eg $[M(O)(O_2)_2\ C_5H_4NCOO]^-$. $2C_5H_4NCOOH$. H_3O^+ (M=Mo and W). The molybdenum peroxo complexes, $[Mo(O)(O_2)C_5\ H_4NCOO]\ H_3O^+$ and $[Mo(O)(O_2)C_5H_3N(COO)_2]H_2O$ have been used as catalysts for the Bayer-Villiger oxidation of cyclic ketones by H_2O_2(90%) to lactones and their derivatives. Using the peroxo complex $[Mo(O)(O_2)C_5H_3N(COO)_2]\ H_2O$ as oxidant and cyclopentanone as substrate, Jacobson *et al.*[46] obtained δ-valerolactones (45%) and 5-hydroxypentanoic acid (15%)



[20]

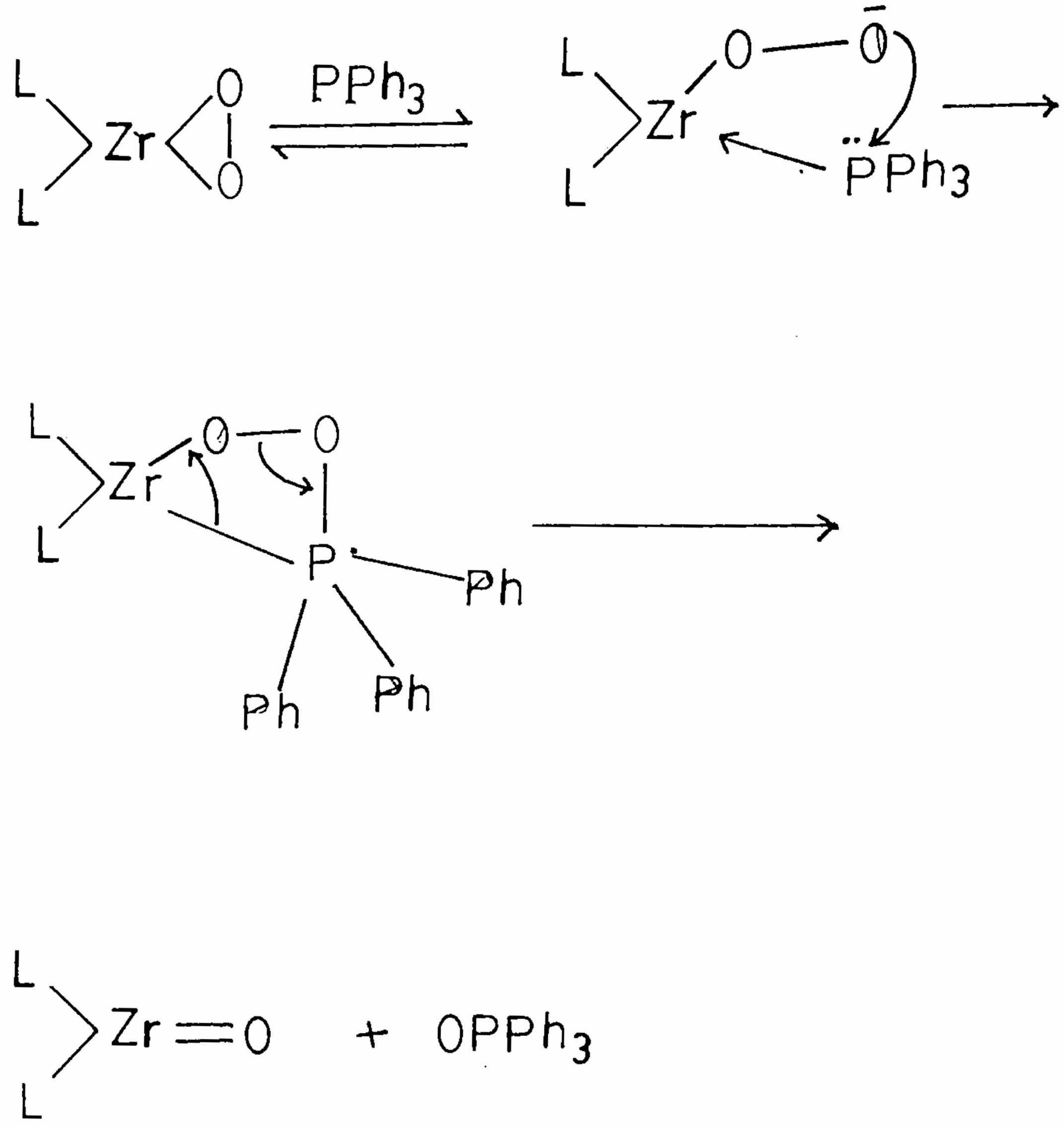
The suggested mechanism involved the formation of the peroxo-metallocycle via the insertion of the carbonyl bond between the M-O bond, just as the proposed mechanism for the epoxidation of olefines. It has been reported that the peroxo complexes containing monodentate ligands such as $Mo(O)(O_2)_2$ HMPA. H_2O decompose readily and are not suitable as catalysts for oxidation of cyclic ketones; however, peroxo complexes stabilized by polydentate ligands are being used as successful oxidants. Besides, the complexes $[M(O)(O_2)_2C_5H_4NCOO]^-H_3O^+$ (M = Mo,W) oxidize secondary alcohols to ketones.

Tarafder *et al.*[93] prepared several zirconium peroxo complexes containing mono,di- and tridentate ligands. These complexes were found to oxidise triphenyl phosphine or triphenyl arsine to their oxides. A possible reaction path which was shown is described in scheme 3.

Tarafder *et al.*[94] prepared some peroxo complexes of group 4A ad 6A metals containing nitrogen-sulfur donor ligands. They found that Mo(VI) complexes were not reactive toward allyl alcohol. But complexes of zr(IV) and Th(IV) were found to oxidize triphenyl phosphine and triphenyl arsine to their oxides.

Dengel *et al.*[95] prepared a number of new stable carboxylato peroxo complexes and presented spectroscopic data for them in the solid state and in solutions. They reported for the first time the X-ray crystal structure of a glycolato peroxo complex. They found that carboxylato ligands capable of forming five membered rings with the metal [eg, oxalate, citrate, tratarate, malate, tartronate, glycolate, quinate, 1, 3 5- tetrahydroxy-cyclohexane carboxylate] generally give stable complexes with peroxo coligands. But carboxylates which did not form such rings (eg. acetate adipate, succinate, salicylate etc) did not form such complexes. The formation of the peroxo complexes also depended on pH.

Tarafder[97] reported some adduct type hexacoodinated peroxo complexes of thorium with the molecular compositions $[The(A\text{-}B\text{-}C)O_2L]$ [A-B-C = pyridine 2, 6-dicarboxylate ligand, L = triphenyl phosphine oxide, arsine oxide etc). The compounds were very stable and failed to oxidise



$L = C_5H_4NCO\bar{O}$

SCHEME 3

allyl alcohol.

Tarafder *et al.*[98] reported the peroxo complexes of Zr(IV) W(VI), and U(VI) ions containing multidentate ligands, eg. EDTA. They showed that the complexes were very stable and were inactive towards oxidation of allyl alcohol, triphenyl phosphine or arsine.

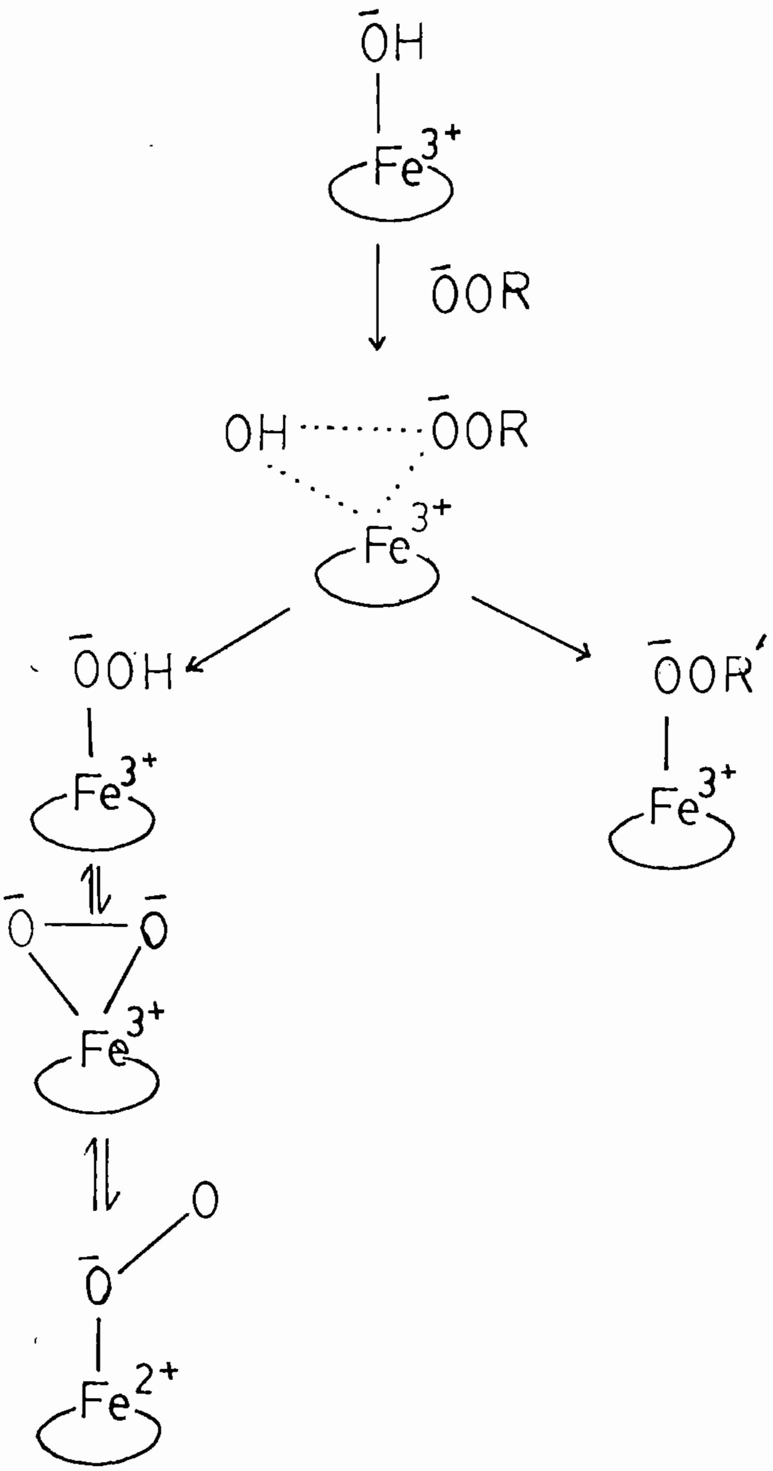
Dengel *et al.*[99] studied the transition metal peroxo complexes of niobium(V) tantalum(V), zirconium(IV) and hafnium(IV) containing carboxylato ligands eg glycolate, citrate etc. They found that reaction of aqueous solutions of the tetraperoxo species $K_3[M(O_2)_4]$, [M = Nb and Ta] with the carboxylic acid in 1:1 ratio in the presence of an excess of H_2O_2 leads to the new complexes of the type $K_3[M(O_2)_3(glyc)].2H_2O$. and $K_3[Nb(O_2)_3(mal)].2H_2O$. The presence of excess of H_2O_2 in the reaction mixture served to increase the yield of the product.

Ghiron *et al.*[100] studied the kinetics of the oxygen transfer reactions of diperoxo and monoperoxo complexes of some metals. They observed that oxodiperoxo complexes were much more reactive than the monoperoxo forms.

Bhattacharjee *et al.*[101] examined the reactivities of $[Zr(O)(O_2)F_2]^{2-}$ and $[Zr(O)(O_2)_2F]^{3-}$. The complexe $[Zr(O)(O_2)F_2]^{2-}$ ion reacted with $SO_2(g)$ in aqueous medium to afford the ternary $[Zr(O)(SO_4)F_2]^{2-}$ complex through insertion of SO_2 into O–O bond.

Fujii *et al.*[102] gave EPR evidence of intermediate peroxo complexes formed in a SOD model system. They proposed the following mechanism for Fe–EDTA peroxo complex, scheme 4.

Chen *et al.*[103] examined the dioxygen adducts of Ni(II) and Co(II) dioxopentaza-macrocycle complexes and summarised their results as (i) Ni–


$\bar{O}H$
Fe^{3+}
$\bar{O}OR$
OH
$\bar{O}OR$
Fe^{3+}
$\bar{O}OH$
$\bar{O}OR'$
Fe^{3+}
Fe^{3+}
$\bar{O}$
$\bar{O}$
Fe^{3+}
O
$\bar{O}$
Fe^{2+}

SCHEME 4

complexes of the above ligands formed short lived dioxygen adducts as do their Co (II) analogues; (ii) the dioxygen affinities of Co (II) complexes were considerably higher than the corresponding Ni (II) Complex, (iii) dioxygen complex formation was strongly exothermic and involved large negative entropy change, (iv) substitution of alkyl and aralkyl groups at the 15 - position slowed the rate of degradation of the dioxygen complexes of both Co (II) and Ni (II).

Tarafder *et al.*[125] examined some peroxo complexes of Cr(VI). Mo(VI), W(VI) and Zr(IV) ions containing tridentate and quardridentate neutral ligands. They showed that the complexes were inert towards oxidation of triphenyl phosphine or arsine due to the enhance stability of the metal peroxo moiety in the presence of tridentate or quardridentate ligands which precludes oxygen transfer reaction.

Islam *et al.*[126] studied some peroxo complexes of Mo(VI) and W(VI) with a dinegative bi-dentate and a neutral bidentate ligands and found that the complexes were inert towards oxidation of olefinic compounds but can oxidize PPh_3 and $AsPh_3$ to their oxides.

Islam *et al.*[129] synthesized some mixed ligand complexes of Zr(IV) and Th(IV) ions containing bidentate organic ligands. Zirconium complexes were found to be inert towards oxidation of allyl alcohol but can oxidize triphenyl phosphine and triphenyl arsines whereas the thorium complexes were active towards oxidation of PPh_3 and $AsPh_3$ as well as allyl alcohol.

CHAPTER 2

EXPERIMENTAL TECHNIQUES.

In this chapter experimental techniques other than the methods of preparation of the complexes will be discussed.

2.1. CLEANING OF GLASS WARES

Glass wares were cleaned in an acid bath, a hot mixture of sulfuric acid and nitric acid. The acid was removed with tap water and then washed with distilled water. These were then dried in an oven at 180°C for 2–3 hours.

2.2. MATERIALS

2.2.1: Zr(IV), Th(IV), U(VI), Mo(VI) and W(VI) compounds.

Zirconium nitrate, tetra-hydrate, $Zr(NO_3)_4.4H_2O$, Thorium nitrate tetra-hydrate, $Th(NO_3)_4.4H_2O$ Uranyl nitrate hexa-hydrate, $UO_2(NO_3)_2.6H_2O$. and Tungstic acid, WO_3 were obtained from British Drug House (BDH) and Molybdic acid, MoO_3 from May and Baker (M & B). The chemicals were all analytical grade and were used without any purifications.

2.2.2: Ligands

8-hydroxyquinoline, 2-aminobenzoic acid, 2-aminophenol, pyridine-2-carboxylic acid, quinoline-2- carboxylic acid, Benzil, cyanex-272, diamminoethane, obtained from MERCK, O-phenylene diamine, glycine and hydrazine hydrate from BDH, [15] ane N_4 from ALDRICH and Leucine, Tyrosine, glycine, and phenyl alanine from MCB were all. analytical grade and were used as received.

2.2.3 : Other chemicals

n-hexane, Benzene, Dioxane, Benzyl chloride, dichloro ethane, acetone, triphenyl phosphine, triphenyl arsine, dimethyl formamide, dimethyl sulphoxide, potassium bromide, hydrogen peroxide, phosphorous pentoxide, potassium hydroxide, carbondisulphide, sodium sulphate obtained from MERCK, tetrahydrofuran, n-butanol, trans stilbene, allyl alcohol, Salicylic acid, methanol, glycol, hydrogen bromide from BDH and ether from FLUKA were used as supplied. Absolute alcohol obtained from Carew and CO, Bangladesh was further purified by refluxing first with I_2 and Mg-turnings for 2½ hours and distilled.

2.3 : PHYSICAL MEASUREMENTS

2.3.1: Conductivity

(i) The conductivities of 10^{-3}M solutions of the complexes (CHAPTER-3) in N, N-dimethyl formamide (DMF) were measured at 298k with a conductivity bridge type MC 3 (Electronic switchgear Ltd. London).

(ii) The conductivities of 10^{-3}M solutions of the complexes (CHAPTER 4-10) in dimethyl sulphoxide (DMSO) were measured at 298 k using a WPA CM 35 conductivity meter and dip type cell with platinized electrodes.

2.3.2: Infrared spectra

IR spectra in the range (4000-200) cm^{-1} (as KBr pellets) of the complexes were recorded with a Pye-Unicam SP3-300 IR spectro-photometer and Acclab 10 (4000–200) cm^{-1} spectrophotometer.

2.3.3: Nuclear magnetic resonance (nmr) spectra

Proton NMR ^1H of some of the complexes were obtained from the department of Chemistry. University of Ottawa, Ottawa, Canada.

2.3.4: Mass spectra

Mass spectra of some complexes were obtained from the Chemistry Department, University of Ottawa, Canada.

2.3.5: Elemental analyses

(i) Carbon and hydrogen analyses for the compounds discussed in CHAPTER-3 were done by Mikroanalytisches labor Pascher Germany.

(ii) Carbon, hydrogen and nitrogen analyses for the complexes discussed in CHAPTERS (4-8) were carried out by Microanalytical services,at the University of St. Andrews, Scotland. Some of the complexes were analyzed by the Regional Sophisticated Instrumentation centre (RSIC), Lucknow, India.

2.3.6: Metal estimation

Metals in some complexes were determined gravimetrically[105].

2.3.7: Estimation of the number of active oxygen atoms in some of the *peroxo* complexes

A known quantity of the sample (0.5–1 g) was dissolved in a minimum volume of methanol (*Ca* 100–150 cm^3) which was acidified with 25 cm^3 of 2N Sulfuric acid and was followed by the successive addition of three drops of osmic acid and one drop of ferroin as an indicator. It was then titrated against previously standardized cerric sulfate solution (*Ca* 0.1N) until there was transition from orange-red to very pale blue color of the solution. As_2O_3 (0.1N) solution was used to standardise cerric sulfate solution.

CHAPTER 3

SOME ORGANOPEROXO COMPLEXES OF MOLYBDENUM AND TUNGSTEN.

3.1 : **Abstract :** Several New peroxo complexes of molybdenum and tungsten containing different organic ligands have been prepared. The complexes have the compositions $[Mo(O)(O_2)L_2]$, $[Mo(O)_2(O_2)L(H_3O)]^+$, $[Mo(O)(O_2)L']$ and $[W(O)(O_2)L_2]$ [L = oxoquinolino, aniline-2-carboxylato, 2-aminophenoxido, picolinato or 2-carboxylatoquinolino ligand; L′ = N-(2-oxophenyl) salicylidenimino ligand], respectively. The complexes were found to oxidise allyl alcohol, and also triphenyl phosphine and triphenyl arsine to their oxides. The IR spectra of the complexes indicate that the frequency of the ν_1-mode of the $M(O_2)$ grouping which is essentially an O-O stretch, decreases with the increase in the atomic number of metals in a particular group.

3.2 : EXPERIMENTAL

3.2.1: Preparation of the Schiff base L′, N-(2-oxophenyl) Salicylidenimine.

A solution of 2-aminophenol (0.1 mol, 10.9 g) in a 1:1 mixture of benzene and ethanol (100 cm^3) was added to a solution of salicylaldehyde (0.1 mol, 12.2 g) in benzene (20 cm^3). The resulting mixture was boiled for 3 minutes and then cooled in an ice salt bath where upon brown reddish yellow crystals formed; these were separated, washed several times with hot ethanol and dried *in vacuo* over magnesium perchlorate. It was recrystallised from methanol. Yield 16 g. Anal. Calcd. for $C_{13}H_{11}NO_2$ C, 73.23% H, 5.16% Found C, 73.23% H, 5.16%

3.2.2: General method for the preparation of complexes (1,3,4,6, and 7) : $[M(O)(O_2)L_2]$ [M = Mo(VI) or W(VI).

A suspension of MO_3(0.013 mol) in 30% H_2O_2(50 cm^3) was stirred overnight at 45–50°C to get a clear solution. This was cooled to 0°C when a solution of organic ligand L (0.026 mol) in acetone (20 cm^3) was added to it. The mixture was stirred while cooling at the same time in an ice-salt bath. A bright yellow precipitate appeared, which was washed successively with water and n-hexane, and dried *in vacuo* over P_4O_{10}.

3.2.3: Preparation of the complex 2 : $H^+[Mo(O)_2(C_6H_4NH_2COO)(H_2O)]$.

The same procedure was applied to (0.0153 mol, 2.2 g) of molybdic acid and (0.0153 mol, 2.1 g) of 2-aminobenzoic acid, yield was 3.0 g (62%).

3.2.4: Preparation of the complex 5 : $[Mo(O)(O_2)C_{13}H_9NO_2]$.

This was also prepared by the same method from molybdic acid (0.01 mol, 1.5 g) and the Schiff base N-(2-hydroxyphenyl) salicylidenimine (0.01 mol, 2.4 g), yielded 2.5 g (67%) of the complex.

3.3 : REACTIVITIES OF THE COMPLEXES

3.3.1: Reaction of 1 with allyl alcohol (Reaction A) :

Compound 1 (0.015 mol, 6.5 g) was suspended in 20 cm^3 of tetrahydrofuran (THF) and a stoichiometric amount of allyl alcohol was added. The mixture was refluxed at 60°C for 24 h. Microdistillation under *ca.* 19 mm Hg yielded glycidol [5 g (57%)] at 145–150°C. The glycidol was identified from its boiling point (160–161°C).

3.3.2: Catalytic reaction of 1 and H_2O_2 with allyl alcohol (Reaction B):

A 25 cm^3 quantity of allyl alcohol (0.376 mol, 21.3 g) was dissolved in 20 cm^3 of dioxane and 1.1 g of 1. was added followed by the addition of 25 cm^3 of 30% H_2O_2. The mixture was kept under reflux at 90°C for 24 h. The reaction mixture was filtered at 19 mm Hg. pressure. The fraction collected at 175-180°C was identified as glycerol. yield 18 g (53%).

3.3.3: Reaction of 3 with triphenyl phosphine (Reaction C) :

A solution of triphenyl phosphine (0.0026 mol, 0.7 g) in THF (20 cm^3) was added to a solution of 3. (0.0026 mol, 0.94 g) in the same solvent (60 cm^3). the mixture was refluxed for 48 h. TLC indicated that the reaction was complete. The solution was filtered and the residue collected. A yellowish white powder was recovered from the filtrate which was identified as $OPPh_3$ [m.p. 155-157°C (lit 157°C)].

3.3.4: Reaction of 4 with triphenyl arsine (Reaction D) :

A solution of triphenyl arsine (0.0022 mol, 0.68 g) in THF (30 cm^3) was added to a solution of 4 (0.0022 mol, 0.86 g) in the same solvent (70 cm^3). The mixture was refluxed for 72 h. TLC indicated that arsine was converted entirely into arsine oxide. The solution was filtered and the residue collected. Evaporation of the filtrate yielded the product [m.p. 187-189°C (lit 189°C)].

Complexes 6 and 7 were also found to be effective stoichiometric reagents for the oxidation of PPh_3 and $AsPh_3$ to their oxides.

3.4: RESULTS AND DISCUSSION

The analytical and molar conductance data (Table 2) are consistent with a seven fold coordination of the metal atom. Titrations of the methanolic solutions of the peroxo complexes with Ce(IV) indicated that 1-7 were mono-peroxo complexes. The molar conductance values indicated that all of the complexes were non-electrolytes in solution except for 2 which exhibited a value characteristic of a 1:1 electrolyte in DMF (Table 2). Literature values[106] for 1:1 electrolytes are comparable to ours. Alkalimetric titration of 2 indicated an inflection point at pH 6.3 which corresponds to the neutralization of the outer-sphere proton.

IR spectral data are shown in Table 3. The ν(O–H) band at 3405 cm^{-1} observed in the free 8-hydroxyquinoline disappears upon coordination, which indicates deprotonation and coordination at the oxygen cite. Further in compound 1 and 7 the decrease in ν(C=N), from the free ligand value (1610 to 1560) and (1610 to 1580) i,e, 50 and 30 cm^{-1} respectively indicates coordination by the heterocyclic nitrogen[39,54,93]. The shifting of ν(C=N) modes thus suggested that Mo(VI) acts as a stronger acceptor than W(VI) Complexes 2 and 3 show two ν(N–H$_2$) bands (Table 3) significantly lower than the values for 2-amino benzoic acid and 2-amino phenol (3390, 3300; 3414, 3342 cm^{-1})[6]. Complexes 2, 4 and 6 show a decrease in ν(C=O) by 48, 85 and 77 cm^{-1} respectively from the free ligand values. (1632, 1640, 1628; 1680, 1725, 1705) cm^{-1} indicating carboxylate binding in the complexes[39,43,55]. In 4 and 6 the appearance of ν(C=N) at 1595 and 1590 cm^{-1} respectively suggest that the heterocyclic nitrogen is coordinated to the metal atom becomes ν(C=N) band in free ligand is 1610 cm^{-1}. The Schiff-base N-(2-hydroxyphenyl)-salicylidenemine in complex 5 be haves as a tridentate-dinegative ligand coordinating at the imino nitrogen and two oxygen atoms[43]. In complex 5 the decrease in ν(C=N) by 25 cm^{-1} relative to the free ligand value[43] indicates coordination through the imino nitrogen atom[86,107]. The ν(O-H) band observed in the free Schiff base at 3290 cm^{-1} disappears upon coordination, which indicates deprotonation and coordination at the oxygen cite. Further support for M-O' (O' = oxygen in organic ligand; M = Mo or W) and M-N bondings in 1-7 are evident from the appearance of ν(M-O') and ν(M-N) modes at 375-405 and 280-312 cm^{-1}, respectively. All of the complexes display ν(M=O) modes[41] at 940-960 cm^{-1} (Table 3).

The metal peroxo grouping gives rise to three IR and Raman active vibrational modes. These are predominantly O-O stretching (ν_1), the symmetric M-O stretch (ν_2), and the antisymmetric M-O stretch (ν_3). The characteristic ν_1 (O-O) modes of 1-6 appear at 848-900 cm^{-1}. There is a decrease in ν_1 upon passing from molybdenum conplexes to the tungsten complexe 7. The ν_1 mode was found to decrease further in the peroxo complexes of uranium[43]. The ν_3 and ν_2 modes in 1-7 appear at 637-680 and 538-612 cm^{-1}, respectively. The assignments shown in Table 3 are based on comparisons with other peroxo complexes of molybdenum and tungsten[39,41,108,109].

3.5 : REACTIVITY

Peroxo complexes of molybdenum and tungsten were not explosive. These were found to liberate iodine on treatment with aqueous iodide. So that the possible reactivity of the present peroxo complexes toward olefinic compounds could be explored.

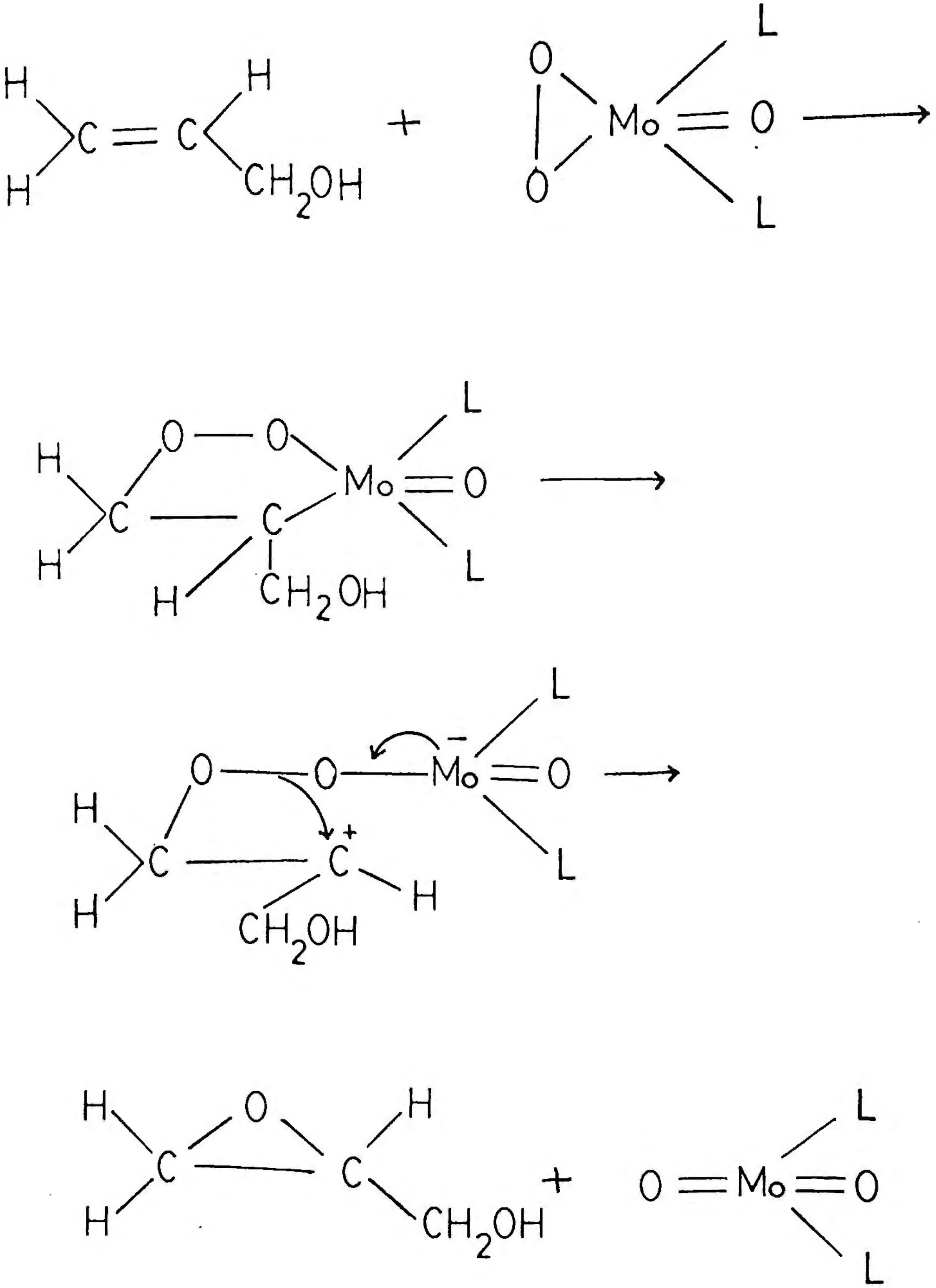
Compound 1 was allowed to react stoichiometrically with allyl alcohol (Reaction A). Which produced glycidol as indicated by an IR band at 1055

cm^{-1} assigned to a C-O-C stretching mode[40,55]. The reaction mechanism has been shown in scheme 5.

With H_2O_2 and using a catalytic amount of 1 (Reaction B) the product isolated was glycerol as indicated by its boiling point. The IR spectrum was identical with that of an authentic sample. The mechanism has been out lined in scheme 6.

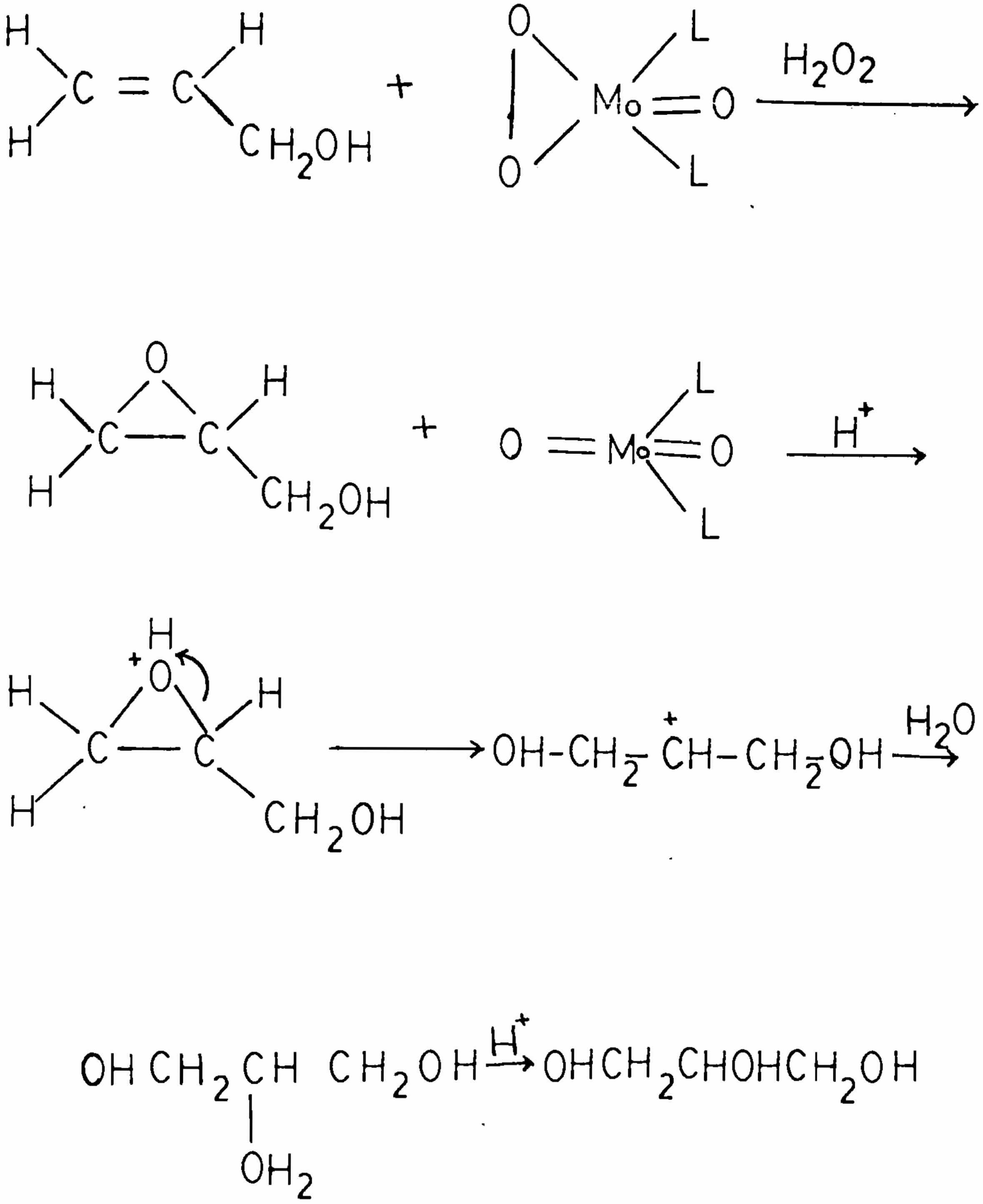
Reactions C and D produced triphenyl phosphine oxide and triphenyl arsine oxide respectively. The products showed IR bands at 1190 and 880 cm^{-1} assigned to ν(P=O) and ν(As=O) modes respectively[110,111]. The reaction path ways has been shown in scheme 7.

IR spectra of the metal residues of reactions C and D showed the disappearance of ν_1(O-O) bands thereby indicating the transfer of peroxo oxyens to the substrates.



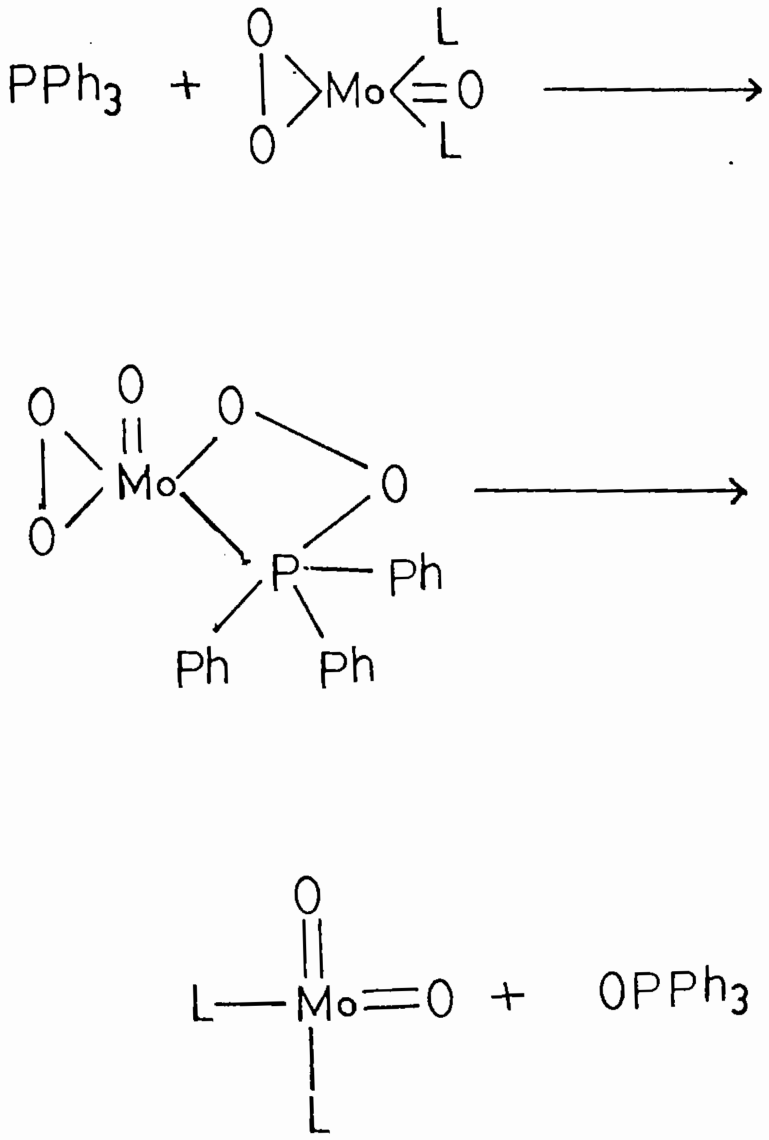
$L = C_9H_6NO$

SCHEME 5



$L = C_9H_6NO$

SCHEME 6



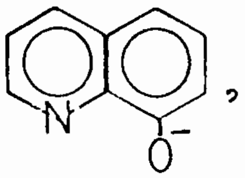
L = $C_6H_4NH_2O$

SCHEME 7

Table 2. Analytical data and other physical properties of Mo(VI) and W(VI) peroxo complexes.

No.	Compound	% metal		% carbon		% hydrogen		% peroxide		Molar conductace ohm^{-1} cm^2 mol^{-1}
		calc.	Found	calc.	Found	calc.	Found	calc.	Found	
1	$[Mo(O)(O_2)(C_9H_6NO)_2]$	22.2	22.0	50.0	50.0	2.8	2.7	7.4	7.4	0
2	$H^+[Mo(O)_2(O_2)(C_6H_4NH_2COO)(H_2O)]$	30.5	30.3	26.6	26.5	2.8	2.8	10.2	10.2	65.5
3	$[Mo(O)(O_2)(C_6H_4NH_2O)_2]$	26.6	26.6	40.0	39.8	3.3	3.3	8.9	8.9	0.2
4	$[Mo(O)(O_2)(C_5H_4NCOO)_2]$	24.6	24.4	36.9	36.8	2.0	2.0	8.2	8.2	0.2
5	$[Mo(O)(O_2)(C_{13}H_9NO_2)]$	25.8	25.6	42.0	41.8	2.4	2.4	8.6	8.6	0.5
6	$[Mo(O)(O_2)(C_9H_6NCOO)_2]$	19.6	19.6	49.2	49.1	2.5	2.4	6.5	6.5	0
7	$[W(O)(O_2)(C_9H_6NO)_2]$	35.4	35.3	41.5	41.3	2.3	2.3	6.1	6.1	0

The organic moieties for the compounds indicated are :



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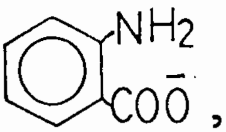

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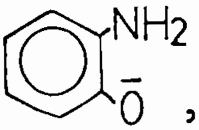

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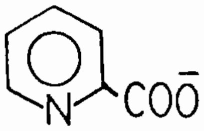

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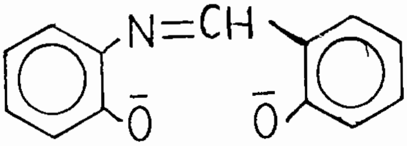

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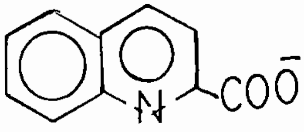

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Table 3. IR spectral data for the Mo(VI) and W(VI) complexes[a] [band maxima ($\mathrm{cm^{-1}}$)].

Compound	ν(O-H)	$\nu(\mathrm{NH_2})$	ν(C=O)	ν(C=N)	ν(M=O)	ν_1(O-O)	$\nu_3(\mathrm{M}<^{\mathrm{O}}_{\mathrm{O}})$	$\nu_2(\mathrm{M}<^{\mathrm{O}}_{\mathrm{O}})$	ν(M-O′)	ν(M=N)
1				1650s	950s	848vs	637vs	538s	400w	312s
2	3400br	3270m 3175m	1632vs		945s	860vs	660s	550vs	375m	290sh
3		3315m 3260m			947s	850vs	640s	590m	400w	280w
4			1640vs	1595m	955s	870s	650vs	600w	400vs	300m
5				1615m	950s	900s	680m	600m	385s	295m
6			1628vs	1590s	960s	865s	670s	612m	405m	285m
7				1580s	940vs	825vs	645s	575m	400w	270m

[a] Relative band intensities are denoted by vs, s, m, w, sh and br, meaning very strong, strong, medium, weak, shoulder and broad respectively.

CHAPTER 4

PEROXO COMPLEXES OF Zr(IV), Th(IV), Mo(VI) AND U(VI) IONS CONTAINING SOME BIDENTATE ORGANIC LIGANDS.

4.1: Abstract:- Several new organo peroxo complexes of Zr(IV), Th(IV), Mo(VI) and U(VI) ions have been prepared and characterised. The complexes have the general formula $[Zr(O_2)C_6H_4(CO_2)_2 .\ 2C_6H_5NO]$, $[Th(O_2)_2L]$ $[Th(O_2)C_6H_4(CO_2)_2\ 2OPPh_3]$, $[Th(O_2)L'_2]$, $[Mo(O_2)_2L]$, $[Mo(O_2)L'_2]$ and $[Mo(O_2)L''H_2O]$

[L = bidentate-neutral ; L′ = bidentate-uninegative and L″ = bidentate-dinegative ligands ; M = Mo(VI) or U(VI)] respectively. Some of the complexes were found to oxidise triphenylphosphine and triphenyl arsine to their oxides. The IR spectra of the complexes indicate that the frequency of the ν_1 mode of the $M(O_2)$ grouping which is essentially an O-O stretch, decreases with the increase in the atomic number of metals in a particular group.

4.2: EXPERIMENTAL

4.2.1: Preparation of Complex 1 : $[Zr(O_2)C_6H_4(CO_2)_2\ 2C_6H_5NO]$.

$Zr\ (NO_3)4.\ 4H_2O$ (0.005 mol) in water (25 cm^3) was added to a solution of phthalic acid (0.005 mol) in methanol (20 cm^3). To the mixture 25 cm^3 of 30% H_2O_2 was added followed by the addition of a solution of C_6H_5NO (0.01 mol) in acetone (50 cm^3). The resulting precipitate which separated out was filtered, washed with ethanol and dried *in vacuo* over P_4O_{10}.

4.2.2: Preparation of the complexes 2 and 3: [Th $(0_2)_2$ L] [L = $C_6H_4(NH_2)_2$ and $C_6H_4NNH_2$].

Th $(No_3)_4$.$4H_2o$ (0.005 mol) in water (25 cm^3) was added to a solution of ligand L(0.005 mol) in ethanol (25 cm^3). To the mixture 30 cm^3 of 30% H_2O_2 was added. The resulting mixture was heated on a steam bath for 10 min. The precipitate so obtained was processed and collected as before.

4.2.3: Preparation of the complexes 4 and 5. $Mo(O)(O_2)(NH_2CH_2CH_2O)_2$ and $[Mo(O)(O_2)(CH_2CH_2O_2)H_2O]$

MoO_3 (0.005 mol) was stirred and heated in 30% H_2O_2 (60 cm^3) at 50°C for 48h. The solution was filtered and the filtrate was added to a solution of stoichiometric amount of organic ligands in ethanol (25 cm^3). The precipitate obtained was separated and stored as above.

4.2.4: Preparation of the complex 6 $[U(O)(O_2)(C_6H_4NH_2O)_2]$.

To a solution of $UO_2(NO_3)2$. $6H_2O$ (0.005 mol) in ethanol (20 cm^3), was added successively a solution of the ligand (0.01 mol) and 25 cm^3 of 30% H_2O_2 which yielded the product. It was separated and stored as above.

4.2.5: Preparation of the complex 7. $[U(O)(O_2)CH_2(CO_2)_2H_2O]$:

To a solution of $UO_2(NO_3)_2$. $6H_2O$ (0.005 mol) in ethanol (20 cm^3) was added successively a solution of the ligand (0.005 mol) in ethanol (25 cm^3) and 30% H_2O_2 (20 cm^3). The resulting precipitate was filtered, washed and stored as above.

4.3: REACTIVITIES OF THE COMPLEXES.

4.3.1: Reaction of 1 with triphenyl phosphine

Triphenyl phosphine (0.004 mol) in THF was added to a suspension of 1 (0.004 mol) in the same solvent. Refluxing the mixture for 48h failed to produce any reaction. The complex was recovered unchanged.

4.3.2: Reaction of 2 with triphenyl arsine

A solution of triphenyl arsine (0.0009 mol, 0.28 g) in THF (25 cm^3) was added to a suspension of the complex (0.00045 mol) in the same solvent. The mixture was refluxed for 48h. TLC indicated that arsine was converted entirely to arsine oxide. The solution was filtered and the residue collected Evaporation of the filtrate yielded the product m.p. 186–188°C (lit value for OPh_3A_s) 189°C)

4.3.3: Reaction of 7 with allyl alcohol.

Refluxing 7 with allyl alcohol in presence of large excess of 30% H_2O_2 in dioxane medium for 48h at 90°C failed to produce any reaction. The unaltered complex 7 was recovered.

4.4: RESULTS AND DISCUSSION

Elemental analyses and conductivity data of the complexes (1–7) were presented in Table 4. The conductivity data for solution in DMSO indicated that 1–7 were all non-electrolytes. IR spectral data were shown in Table 5. Complex of phthalic acid 1 showed a decrease of ν(c=o) by 22 cm^{-1} (1658 cm^{-1}) compared to the free ligand value (1680 cm^{-1}) and those of malonic acid showed a decrease of ν(c=o) by 87 cm^{-1} (1638 cm^{-1}) compared to the free ligand value (1725 cm^{-1}) indicating carboxylate binding in the complex. In complex 1 complexing causes a decrease in ν(N-O) by 32 cm^{-1} (1210 cm^{-1}) compared to the free pyridine oxide (1242 cm^{-1}). Ethylene glycol is potentially bidentate, dinegative. The ν(OH) mode, observed as a broad band at 3200–3600 cm^{-1} disappeared upon co-ordination in 5 which indicated deprotonation and co-ordination at the oxygen site. Complexes 2, 3, 4 and

6 showed two bands, (2; 3340 and 3280); (3, 3280 and 3180); (4, 3200 and 3140); and (6, 3220 and 3165 cm^{-1}) significantly lower than the values for O-phenylenediamine (3400, 3380 cm^{-1} in 2); 2-aminophyridine (3350, 3200 cm^{-1} in 3); 2-aminophenol (3414, 3342 cm^{-1} in 6) and ethanol amine (3380, 3290 cm^{-1} in 4). This was also evident from the appearance of bands at 255-320 cm^{-1} which were tentatively attributed to the ν(M-N) modes. M=Zr(IV). Th(IV), Mo(VI) and U(VI).

Further in complex 3 the ν(C=N) mode appeared at 1570 cm^{-1} indicating that the ring nitrogen is coordinated to the metal atom[54]. In addition, the far IR spectra of 1, 4, 5, 6 and 7 display bands at 360-460 cm^{-1} (Table 5) which were tentatively attributed to the ν(M-O′) modes[43,55,93,94,96,97] (O′= oxygen in the organic ligands). The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman active vibrational modes. These were predominantly (O-O) stretching (ν_1) the symmetric M-O stretch (ν_2) and the antisymmetric M-O stretch (ν_3). The characteristic ν_1(O-O) mode of 1-7 appeared at 800-875 cm^{-1} (Table 5). In particular the ν_1 mode of the present thorium peroxo complexes (2-3) occurred at slightly lower frequencies than the zirconium analogue (1). This was more discernible in the peroxo complexes of the elements of group 6A; there is a decrease in ν_1 upon passing from molybdenum complexes (4-5) (865-875 cm^{-1}) to the corresponding uranium peroxo complexes (6-7) (800-830 cm^{-1}). The present data, thus showed that for the M(O_2) grouping the ν_1(O-O) mode decreased with the increase in the atomic number of metals in a particular group. In the present examples the ν_3 and ν_2 mode appeared at 600-695 and 500-555 cm^{-1} respectively. These assignments were based on comparison with other peroxo complexes of zirconium, thorium, molybdenum and uranium[55,93,94,96,97,108,109]. The complexes (4-7 display ν(M=O) modes[41,96] at 900-925 cm^{-1}. Complexes 5 and 7 showed broad bands at 3160 cm^{-1} arising from coordinated water molecules.

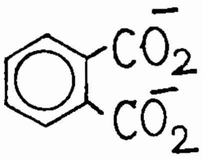
4.5: REACTIVITY

These peroxo complexes were not explosive so that the possible reactivity of the complexes towards olefinic compounds and towards triphenyl phosphine and arsine could be explored. Compound 2 was allowed to react with $AsPh_3$. The reaction produced $OAsPh_3$. The product showed IR bands at 880 cm^{-1} assigned to ν(As=O) mode[12,15]. Compound 7 was allowed to react with allyl alcohol. The compound failed to oxidize allyl alcohol even when refluxing at 90°C was continued for 48h. Compound 1 also failed to oxidize PPh_3 when refluxed in THF medium for 48h. The negative result outline the enhanced stability of the metal peroxo moiety in the presence of bidentate, dinegative chelating ligands. We observed similar negative results with other peroxo complexes containing tridentate, bidentate-dinegative and quardridentate ligands[55,93,97,98].

Table 4. Analytical data and other physical properties of the peroxo complexes[a].

No.	Compound	Colour	% metal		% carbon		% hydrogen		Molar conductance $\Omega^{-1}cm^{2}\ mol^{-1}$
			calc.	found	calc.	found	calc.	found	
1.	$[Zr(O_2)C_6H_4(CO_2)_2.2C_5H_5NO]$	Ash	19.1	19.1	45.3	45.2	2.9	2.9	0
2.	$[Th(O_2)_2C_6H_4(NH_2)_2]$	Ash	57.4	57.2	17.8	17.5	1.9	2.0	1.5
3.	$[Th(O_2)_2(C_5H_4NNH_2)$	Yellow	59.5	59.1	15.4	15.4	1.5	1.5	0
4.	$[Mo(O)(O_2)(NH_2CH_2CH_2O)_2]$	Yellow	36.3	36.4	18.2	18.1	4.5	4.4	0
5.	$[Mo(O)(O_2)(CH_2CH_2O_2)H_2O]$	Black	43.2	43.3	10.8	10.8	2.7	2.7	2.5
6.	$[U(O)(O_2)(C_6H_4NH_2O)_2]$	Yellow	47.4	47.5	28.7	28.7	2.4	2.4	1.5
7.	$[U(O)(O_2)CH_2(CO_2)_2H_2O]$	Yellow	58.6	58.7	8.9	8.8	0.98	0.9	0

[a] The organic moieties for the compounds indicated are



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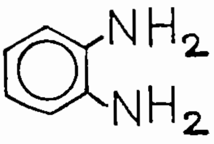

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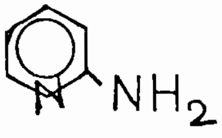

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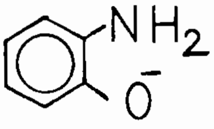

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$NH_2CH_2CH_2\bar{O}$

4

$\bar{O}CH_2CH_2\bar{O}$

5

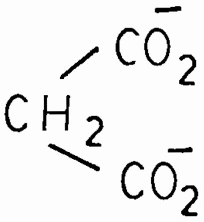

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Table 5. IR spectral data for the Zr(IV), Th(IV), Mo(VI) and U(VI) complexes[a] [band maxima (cm^{-1})].

Compound No.	ν(O-H)	ν(NH_2)	ν(C=O)	ν(C=N)	ν(E=O)	ν(M=O)	ν_1(O-O)	$\nu_3\left(\mathrm{M}\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\right)$	$\nu_2\left(\mathrm{M}\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\right)$	ν(M-O′)	ν(M-N)
1.			1658vs		1210sh		832vs	675vs	555vs	425vs	
2.		3340w 3280w					828vs	600w	525w		320sh
3.		3280w 3180w		1570w			830s	600w	525w		310sh
4.		3200w 3140w				900vs	870sh	635m	530m	400w	300w
5.	3160br					925vs	870sh	635vs	530vs	390s	
6.		3220w 3165w				905vs	810w	600sh	540w	640br	260sh
7.	3160br		1638vs			920vs	815m	600br		405m	

[a] Relative band intensities are denoted by vs, s, m, w, sh and br meaning very strong, strong, medium, weak, shoulder and broad respectively.

CHAPTER 5

PEROXO COMPLEXES OF ZIRCONIUM(IV), THORIUM(IV), MOLYBDENUM(VI) TUNGSTEN(VI) AND URANIUM(VI) CONTAINING TWO QUADRIDENTATE ONNO SCHIFF BASES.

5.1: Abstract: Some new peroxo complexes of molybdenum, tungsten, uranium, zirconium and thorium containing quardridentate, dinegative schiff base ligands have been synthesized and characterized. The schiff bases $C_{20}H_{14}N_2O_2H_2$ and $C_{14}H_{10}N_2O_2H_2$ were derived from the condensation of O-phenylenediamine or hydrazine hydrate with salicylaldehyde, respectively. The schiff bases undergo deprotonation, while complexation having ONNO donor sequences producing complexes of compositions $[M(O)(O_2)(ONNO)]$ and $[M'(O_2)(ONNO)]$ [M = Mo^{VI}, W^{VI} and U^{VI}; M′ = Zr^{IV} and Th^{IV}, ONNO = $C_{20}H_{14}N_2O_2^{2-}$ and $C_{14}H_{10}N_2O_2^{2}$]. The chelate effect of the quardridentate ligands stabilizes the metal-peroxo moiety which prevents oxygen transfer reactions to both organic and inorganic substrates. The σ donor nature of the quardridentate ligands influences the mode of coordination of the peroxo moiety. The frequency of the v_1 mode of the $M(O_2)$ grouping decreases with an increase in the atomic number of the metals in a particular group.

5.2: EXPERIMENTAL

5.2.1: Preparation of the schiff base $C_{20}H_{14}N_2O_2H_2$:

Salicylaldehyde (0.01 mol, 1.22 g) in absolute ethanol (30 cm^3) was added to a solution of O-phenylenediamine (0.005 mol, 0.54 g) in the same solvent (20 cm^3). The mixture was boiled down to ca 25 cm^3 and cooled to room temperature. The orange-red crystal which separated were washed with ethanol. Melting point 142-144°C (Found : C, 75.8; H, 4.9; N,8.8 Calc for C_{20} H_{14} N_2O_2 H_2 : C, 75.9; H,5.1; N, 8.9%).

5.2.2: Preparation of the schiff base $C_{14}H_{10}N_2O_2H_2$:

Salicylaldehyde (0.01 mol, 1.22 g) in absolute ethanol (30 cm^3) was added to a solution of hydrazine hydrate (0.005 mol, 0.25 g) in the same solvent (15 cm^3). The mixture was heated on a water bath to reduce the volume to *ca* 20 cm^3 and cooled to room temperature. The yellow crystals were separated and washed with ethanol. melting point 209-211°C (Found: C, 69.9; H, 4.9; N.11.7. calc for C_{14} H_{10} N_2 O_2 H_2 C, 70.0; H, 5.0; N, 11.7%

5.2.3: General methods for the preparation of complexes 1, 3 and 4: $[M(O)(O_2)L.]$ (M = Mo^{VI} and W^{VI}; L = $C_{20}H_{14}N_2O_2^{2-}$or $C_{14}H_{10}N_2O_2^{2-}$

A suspension of MO_3 (0.017 mol) in 30% H_2O_2 (60 cm^3) was stirred over night at 45-50°C. This was filtered and to the clear filtrate was added a solution of L (0.017 mol) in hot ethanol (150 cm^3). The mixture was stirred whilst cooling at the same time in an ice salt bath. A yellow precipitate appeared, which was washed successively with water and ether and dried in *vacuo* over P_4O_{10}.

5.2.4. Preparation of the complexes 2 and 5: $[U(O)(O_2)L.]$ (L = $C_{20}H_{14}N_2O_2^{2-}$and $C_{14}H_{10}N_2O_2^{2}$):

To a solution of $UO_2(NO_3)_2$ 6 H_2O (0.006 mol) in ethanol (35 cm^3), a solution of L (0.006 mol) in the same solvent (100 cm^3) and then 30% H_2O_2 (35 cm^3) were added. The product was separated and stored as above.

5.2.5: Preparation of the complexes 6 and 7. $[M(O_2)$ L] (M = ZrIV or ThIV L = $C_{20}H_{14}N_2O_2^{2}$]

A solution of $M(NO_3)4$, 6 H_2O (0.005 mol in water (40 cm^3) was added to a solution of L. (0.005 mol) in ethanol (100 cm^3), followed by the addition of 30% H_2O_2 (30 cm^3). The product was separated and stored as above.

5.3: REACTIVITIES OF THE COMPLEXES :

5.3.1: Reaction of 1 with allyl alcohol:

Refluxing of 1 with allyl alcohol in a 1:1 molar ratio in tetrahydrofuran (THF) medium for 48h. failed to produce any reaction; 1 was recovered unchanged.

5.3.2: Reaction of 4 with allyl alcohol in presence of excess of H_2O_2:

The complex 4 was refluxed with allyl alcohol in the presence of a large excess of 30% H_2O_2 in dioxane medium for 48h at 90°C also failed to produce any reaction; 4 was recovered unchanged.

5.3.3: Reaction of 5–7 with triphenyl phosphine and triphenyl arsine:

Complexes 5–7 were refluxed with equimolecular quantities of triphenyl phosphine and triphenyl arsine, respectively in THF for 48h also failed to produce any reaction; 5–7 were recovered unchanged.

5.4: RESULTS AND DISCUSSION

The analytical data was presented in Table 6. The molar conductance values showed that all of the complexes were non electrolytes in DMSO indicating that the chelate anions were covalently bonded in all the cases. These data were consistent with seven fold coordination of molybdenum(VI) tungsten(VI) and uranium(VI) complexes, while the zirconium(IV) and thorium(IV) analogues were hexa coordinated.

IR spectral data were presented in Table 7. The ligands $C_{20}H_{14}N_2O_2H_2$

and $C_{14}H_{10}N_2O_2H_2$ were potentially quardridentate, coordinating via the two methine nitrogen atoms and oxo anions generated during complexation. The free schiff bases produce ν(OH) bands (Table 7.) which disappear in the complexes indicating deprotonation at the OH end, thus providing an oxo coordination. This was also apparent from the non electrolytic nature of the complexes. That the ligands deprotonate at the OH end was also evident from the appearance of ν(M-O′) (O′ = oxygen in organic ligands) modes at 360–435 cm^{-1} (Table 7.) in the far-IR spectra of the complexes[43,55,93,94,96-98,112]. The ν(C=N) bands observed at 1560 and 1570 cm^{-1} for $C_{20}H_{14}N_2O_2H_2$ and $C_{14}H_{10}N_2O_2H_2$ respectively, were shifted to lower frequencies (Table 7.) upon complexation, indicating coordination at the methine nitrogen atoms. This was also apparent from the ν(M-N) modes at 260–350 cm^{-1} in the far-IR spectra of the complexes[45,55,93,94,96-98,112]. The ν(M-N) band[113] observed at 985 cm^{-1} for free $C_{14}H_{10}N_2O_2H_2$ was shifted to lower frequencies in 3–5 indicating that both the azo methine nitrogen atoms were coordinated. Complexes 1–5 show diagnostic bands at 910–925 cm^{-1} attributable to ν(M=O) modes[43,98,112]. The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman active vibrational modes. These were predominantly O-O stretching (ν_1) the symmetric M-O stretch (ν_2) and antisymmetric M-O stretch (ν_3). The characteristic ν_1(O-O) modes of 1–7 appear at 795–840 cm^{-1} (Table 7). In particular, the ν_1 mode decreases upon passing from molybdenum complexes (1 and 3) (840 and 845 cm^{-1}) to the corresponding tungsten complex (4) (825 cm^{-1}), which was then further decreased in the uranium peroxo complexes (2 and 5) (790 and 795 cm^{-1}). The ν_1 mode of the thorium peroxo complex 7 (805 cm^{-1}) appears at a lower frequency than the zirconium analogue (6) (820 cm^{-1}). The present study thus clearly reveals that for the M(O_2) grouping, the ν_1(O–O) modes decrease with an increase in the atomic number of metals in a particular group. Again in the present examples, it was discernible that the ν_1 modes of molybdenum, tungsten, uranium, zirconium and thorium complexes appear at lower frequencies than the peroxo complexes of these metals containing monodentate, bidentate and tridentate auxiliary ligands[41,43,55,93,94,96-98,112]. This was presumably due to a greater charge cancellation of the metal centers by the quardridentate σ–donor ligands, thereby causing a weaker coulombic interaction in the M^{n+}–O_2^{2-}(n = 4 or 6) moiety in the present examples. The present peroxo complexes display ν_3 and ν_2 modes at 602–670 and 520–560 cm^{-1}, respectively (Table 7).

5.5: REACTIVITY

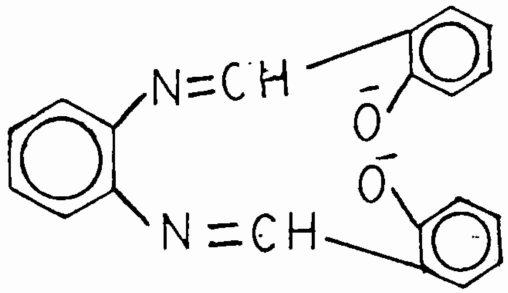
The present peroxo complexes were found to be inert towards oxidation of olefin and other substrates. Complexes 1 and 4 failed to oxidize allyl alcohol even when refluxing at 90°C was continued for 48h. Compounds 5–7 were also unreactive towards phosphine and arsine. These negative results outline the enhanced stability of the metal peroxo moiety in the presence of quardridentate dinegative chelating ligands which precludes oxygen transfer reactions. We also observed a similar stabilizing effect of the peroxo complexes containing various multi - dentate organic ligands[43,55,93,97,98,112].

Table 6. Analytical data and other physical properties of the peroxo complexes[a].

No.	Compound	Colour	% carbon calc.	% carbon Found	% hydrogen calc.	% hydrogen Found	% Nitrogen calc.	% Nitrogen Found	Molar conductance ohm^{-1} cm^2 mol^{-1}
1.	$[Mo(O)(O_2)(C_{20}H_{14}N_2O_2)]$	Yellow	52.4	52.3	3.0	3.0	6.1	6.1	2
2.	$[U(O)(O_2)(C_{20}H_{14}N_2O_2)]$	Yellow	40.0	39.8	2.3	2.3	4.6	4.5	0
3.	$[Mo(O)(O_2)(C_{14}H_{10}N_2O_2)]$	Yellow	44.0	43.9	2.6	2.5	7.3	7.1	5
4.	$[W(O)(O_2)(C_{14}H_{10}N_2O_2)]$	Yellow	35.7	35.7	2.1	2.1	5.9	5.9	1
5.	$[U(O)(O_2)(C_{14}H_{10}N_2O_2)]$	Yellow	32.0	32.0	1.9	1.8	5.3	5.3	0
6.	$[Zr(O_2)(C_{20}H_{14}N_2O_2)]$	Colorless	54.9	54.7	3.2	3.2	6.4	6.0	3
7.	$[Th(O_2)(C_{20}H_{14}N_2O_2)]$	Colorless	51.5	51.5	2.4	2.4	4.8	4.8	0

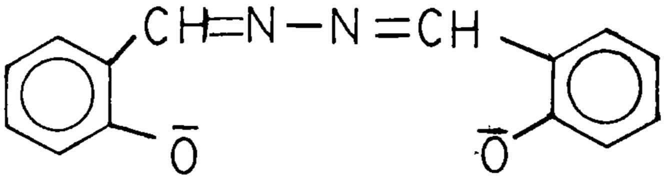
[a] The organic moieties for the compounds are:

$C_{20}H_{14}N_2O_2^{2-}$ =



1, 2, 6, 7

$C_{14}H_{10}N_2O_2^{2-}$ =



3, 4, 5

Table 7. IR spectral data for the Mo(VI), U(VI), W(VI), Zr(IV), and Th(IV) complexes[a] [band maxima (cm^{-1})].

Compound	ν(O-H)	ν(C=N)	ν(N=N)	ν(M=O)	ν_1(O-O)	$\nu_3\left(\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\\ \mid\\ \diagdown\mathrm{O}\end{smallmatrix}\right)$	$\nu_2\left(\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\\ \mid\\ \diagdown\mathrm{O}\end{smallmatrix}\right)$	ν(M-O′)	ν(M-N)
$C_{20}H_{14}N_2O_2H_2$	3600-3300br	1560vs							
$C_{14}H_{10}N_2O_2H_2$	3600-3400br	1570s	985vs						
1.		1510vs		920vs	840vs	615vs	528vs	365s	352m
2.		1520vs		910s	790vs	610s	520vs	420s	260s
3.		1515vs	960s	925s	845s	615s	528s	360s	350m
4.		1525vs	965s	930s	825vs	615s	525s	375s	295m
5.		1530vs	970s	910s	795vs	615s	525m	435s	270m
6.		1520vs			820vs	670m	560m	420s	310w
7.		1530s			805s	602vs	520m	400m	300m

[a] Relative band intensities are derided by vs, s, m, w and br representing very strong, strong, medium, weak and broad respectively.

CHAPTER 6

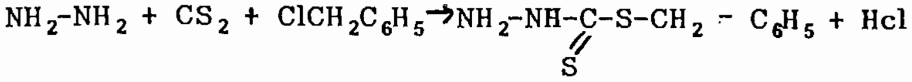
PEROXO COMPLEXES OF ZIRCONIUM(IV), THORIUM(IV), MOLYBDENUM(VI), TUNGSTEN(VI) AND URANIUM(VI) IONS CONTAINING A QUADRIDENTATE SNNS SCHIFF BASE.

6.1: Abstract : New peroxo complexes of zirconium(IV), thorium(IV), molybdenum(VI), tungsten(VI) and uranium(VI) containing a quardridentate schiff base, formed by the condensation of S-benzyldithiocarbazate and benzil have been synthesized and characterized. The complexes have the general formula $[M(O_2)(SNNS)]$ ($M = Zr^{IV}$ and Th^{IV}) and $[M'(O)(O_2)(SNNS)]$ ($M' = Mo^{VI}$, W^{VI} and U^{VI}). These peroxo complexes were found to be inert towards oxidation. The size of the metals as well as the electronic effect derived from the quardridentate schiff base influence the mode of coordination of the peroxo moiety. The frequency of the ν_1 mode of the $M(O_2)$ grouping decreases with an increase in the atomic number of the metals in a particular group and in the δ donor electronic nature of the quardridentate schiff base used.

6.2: EXPERIMENTAL

6.2.1: Preparation of S-benzyldithiocarbazate $NH_2NHCSS\ CH_2C_6H_5$:

S-benzyldithiocarbazate was prepared as follows[114]: Potassium hydroxide (0.20 mol, 11.4 g) was dissolved in 90% ethanol (70 ml). Hydrazine hydrate (0.20 mol 10 gm) was added to it and the mixture was cooled to 0°C in an icc salt bath. Carbon disulfide Cs_2 (0.20 mol, 15.2 g) was added dropwise with constant stirring over a period of 1 h. During this time two layers had formed. The light- brown lower layer was separated and dissolved in cold 40% ethyl alcohol (60 cm^3). The mixture was kept in an ice bath and benzyl chloride (0.20 mol, 25 g) was added dropwise with vigorous stirring of the mixture. After the complete addition of benzyl chloride the white product which had formed was filtered off, washed with water and after drying was recrystallized from benzene and dried over anhydrous calcium chloride yield 12 g.m.p. 125°C. Found C, 48.5; H, 5.0; S, 31.8, calcd for $C_8H_{10}N_2S_2$: C, 48.5; H, 5.1; S, 32.3%



$$NH_2\text{-}NH_2 + CS_2 + ClCH_2C_6H_5 \rightarrow NH_2\text{-}NH\text{-}\underset{\underset{S}{/\!/}}{C}\text{-}S\text{-}CH_2 - C_6H_5 + Hcl$$

6.2.2: Preparation of the schiff base $C_{30}H_{26}N_4S_4$

A solution of S-benzyldithiocarbazate (0.0546 mol, 11.2 g) in absolute ethanol (300 cm^3) was added to a solution of benzil (0.0188 mol 3.9 g) in the same solvent (100 cm^3). The mixture was refluxed for 6h and the yellow crystals which settled on cooling were separated out and washed with ethanol.

Yield 12.2 g. m.p. 168°C (Found C, 63.2; H, 4.6; N, 9.8 calcd for $C_{30}H_{26}N_4S_4$; C, 63.2; H, 4.6; N, 9.8%

6.2.3: Preparation of the complexes 1 and 2 :

[M(O_2)(SNNS)], [M =Zr^{IV} or Th^{IV}, SNNS = $(C_{30}H_{24}N_4S_4)^{2-}$]

The schiff base $C_{30}H_{26}N_4S_4$ (0.0002 mol) was added to a solution of potassium hydroxide (0.0004 mol) in 30% H_2O_2 (20 cm^3). The solution was heated for 5 min filtered and to the filtrate was added with stirring a solution of $M(NO_3)_4.4H_2O$ (0.0002 mol) in water (15 cm^3). The resulting precipitate which separated out was filtered, washed several times with water and dried in *vacuo* over P_4O_{10}.

6.2.4: Preparation of the complexe 3 and 4 : $[M(O)(O_2)(SNNS)]$ [M = Mo^{VI} and W^{VI}]

The schiff base $C_{30}H_{26}N_4S_4$ (0.005 mol) was added to a solution of potassium hydroxide (0.01 mol) in 30% H_2O_2 (100 cm^3). The solution was heated for 5 min, filtered and to the filtrate was added, with stirring, a solution of MO_3 (M = Mo^{VI} and W^{VI} (0.005 mol in 30% H_2O_2 (60 cm^3). The resulting precipitate was filtered, washed successively with water and ether and dried in *vacuo* over P_4O_{10}.

6.2.5: Preparation of the complex 5 : $[U(O)(O_2)(SNNS)]$

The schiff base $C_{30}H_{26}N_4S_4$ (0.005 mol) was dissolved in a solution of potassium hydroxide (0.01 mol) in 30% H_2O_2 (100 cm^3). The solution was heated for 5 min, filtered and to the filtrate was added, a solution of $UO_2(NO_3)_2 \cdot 6H_{2}0$ (0.005 mol) in water (50 cm^3). The solution was boiled and cooled. The resulting precipitate was filtered, washed successively with water and ether and stored as above.

6.3: REACTIVITIES OF THE COMPLEXES :

6.3.1: Attempted reaction of the complex 1 with allyl alcohol

Refluxing the complex 1 with allylalcohol in a 1:1 molar ratio in THF medium for 48 h failed to produce any reaction; 1 was recovered unchanged.

6.3.2: Reaction of 2 with allyl alcohol in presence of excess H_2O_2

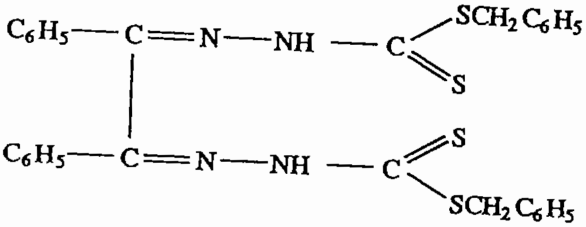
The complex 2 was refluxed with allyl alcohol in presence of large excess of 30% H_2O_2 in dioxane medium of 48 h. at 90°C. It also failed to produce any reaction; 2 was recovered unchanged.

6.3.3: Reaction of 3 and 5 with triphenyl phosphine and triphenyl arsine

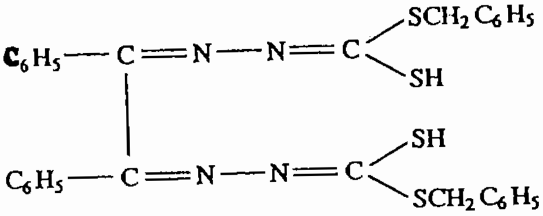
Refluxing 3 and 5 with equimolar quantities of triphenylphosphine or triphenyl arsine respectively in THF for 48h also failed to produce any reaction; 3 and 5 were recovered unchanged.

6.4: RESULTS AND DISCUSSION :

Elemental analyses and conductivity data for the complexes were presented in Table 8. The complexes were non electrolytes in DMSO solution suggesting that the anions were covalently bonded in all the cases. The mass spectrum of the schiff base $C_{30}H_{26}N_4S_4$ did not display the molecular ion peak but showed other diagnostic peaks at m/z 285, 211, 149, 105, 77, 51 and 28.



(Ia)



(Ib)

The schiff base can exist in the thioketo form (1a) or in enethiol form (1b) or as a mixture of both. The IR spectrum of the schiff base did not display ν(SH) at *ca* 2570 cm^{-1} but exhibits ν(NH), ν(C=N) and ν(C=S) modes (Table 9), indicating that in the solid state the schiff base remains in the thioketo from (1a). Its ^{1}H NMR spectrum in $CDCL_3$ exhibits signals at 4.36, 7.5 and 9.89 ppm corresponding to the methylene, phenyl and NHprotons, respectively.

The ^1H NMR spectrum did not display peak attributable to a S-H proton. Therefore the schiff base remains predominantly in the thioketo form (1a) in $CDCl_3$. The schiff base, however forms complexes only in basic medium. Attempts to prepare complexes from a neutral medium were unsuccessful. This suggests that the nucleophilicity of the ligand was greatly enhanced in alkaline medium probably due to the creation of an anionic site in *situ*[114-118]. The thione group was relatively unstable in the monomeric form and undergoes a thione (1a) ⇌ thiol (1b) equilibrium. The deprotonation and consequent formation of an anionic site in *Situ* was favoured by the basicity of the medium and the ν(N-H) and ν(C=S) bands of the free ligand disappear in the spectra of the complexes suggesting that the ligand was coordinated in the deprotonated thiol form. This was also evident from the appearance of ν(C-S)[120-121] bands at 710-725 cm^{-1} and ν(M-S) bands [94,116,117,122] at 225-270 cm^{-1} (Table 9) in the IR spectra of the complexes. The ν(C=N) band of the free schiff base was shifted to lower frequencies in the complexes (Table 9) suggesting that the azomethine nitrogen was coordinated. A molecular model shows that the α-nitrogen (iminonitrogen) was not bonded due to considerable stearic strain[114-118] The far IR spectra of the complexes exhibit bands in the region 300-325 cm^{-1} (Table 9) which are tentatively attributed to ν(M-N) modes[43,55,93,94,96,122,124]. Complexes 3-5 display bands at 915-925 cm^{-1} assignable to ν(M=O) modes[43,98,112]. The metal peroxo grouping (local C_{2v} Symmetry) give rise to three IR and Raman-active vibrational modes. These are predominantly O-O stretching (ν_1), the symmetric M-O stretch (ν_2) and the antisymmetric M–O stretch (ν_3). The characteristic ν_1(O–O) modes of 1-5 appear at 800–840 cm^{-1} (Table 9). In particular, the ν_1 mode decreases from the zirconium complex (1, 820 cm^{-1}) to the corresponding thorium complex (2, 810 cm^{-1}). This was also discernible in the cases of peroxo complexes of the elements of group 6A, There was a decrease in ν_1 upon passing from the molybdenum complex (3, 840 cm^{-1}) to the corresponding tungsten complex (4, 830 cm^{-1}) which was further decreased in the uranium peroxo complexes (5, 800 cm^{-1}). The present data thus clearly reveal that for the $M(O_2)$ grouping the ν_1(O–O) modes decrease with an increase in the atomic number of the metals in a particular group. In the present examples, ν_3 and ν_2 modes appear at 620–650 and 530–550 cm^{-1} respectively. It was noteworthy that the ν_1 mode of the present peroxo complexes of zirconium, thorium, molybdenum, tungsten and uranium appear at lower frequencies than the peroxo complexes of these metals containing monodentate, bidentate and tridentate ancillary ligands[43,55,93,94,96,98,112]. This is presumably due to greater charge neutralization of the metal centres by the quardridentate, dinegative δ-donor ligand, causing a weaker coulombic interaction in the $M^{n+}-O_2^{2-}$ moiety (n=4 or 6).

6.5: REACTIVITY :

The present peroxo complexes were not found to undergo oxygen transfer reactions. Complexes 1 and 2 failed to oxidize allyl alcohol even when refluxing at 90°C was continued for 48h. Complexes 3 and 5 were also unreactive towards phosphine and arsine. These negative results outline the enhanced stability of the metal peroxo moiety in the presence of the quardridentate chelating ligand which precludes oxygen transfer reaction.

Similar results were also found for the peroxo complexes containing tridentate and quardridentate ligands [43,93,97,112]

Table 8. Analytical data and other physical properties of the complexes[a].

No.	Compound	Colour	% carbon calc.	% carbon found	% hydrogen calc.	% hydrogen found	% nitrogen calc.	% nitrogen found	Molar conductance Ω^{-1} cm^2 mol^{-1}
1.	$[Zr(O_2)(SNNS)]$	Ash	52.1	52.0	3.5	3.3	8.1	8.1	0
2.	$[Th(O_2)(SNNS)]$	Colourless	43.3	43.1	2.9	2.8	6.7	6.5	2
3.	$[Mo(O)(O_2)(SNNS)]$	Yellow	50.6	50.3	3.4	3.4	7.9	7.7	1
4.	$[W(O)(O_2)(SNNS)]$	Yellow	45.0	45.0	3.0	3.0	7.0	6.8	0
5.	$[U(O)(O_2)(SNNS)]$	Yellow	42.2	42.1	2.8	2.8	6.6	6.5	4

[a]The organic moiety for the compounds indicated is $(C_{30}H_{24}N_4S_4)^{2-}$

Table 9. IR spectral data for the Zr(IV), Th(IV), Mo(VI) and W(VI) and U(VI) complexes[a] [band maxima (cm^{-1})].

No. compound	ν(N-H)	ν(C=N)	ν(C=S)	ν(C-S)	ν_1(O-O)	$\nu_3(\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix})$	$\nu_2(\mathrm{M}\begin{smallmatrix}\diagup\mathrm{O}\\ \vert\\ \diagdown\mathrm{O}\end{smallmatrix})$	ν(M-M)	ν(M-S)	ν(M=O)
$C_{30}H_{26}N_4S_4$	3285m	1560vs	1045s							
1.		1520s		710vs	820s	650vs	550s	328vs	270vs	
2.		1525s		715vs	810s	625vs	530vs	315s	265s	
3.		1515vs		710s	840vs	620s	535s	300vs	255s	915vs
4.		1525s		720s	830s	630vs	540s	315vs	260s	920s
5.		1530s		725s	800vs	635s	545s	320m	270m	925vs

[a] Relative band intensities are denoted by vs, s and m representing very strong, strong, and medium respectively.

CHAPTER 7

PEROXO COMPLEXES OF MOLYBDENUM(VI) AND URANIUM(VI) IONS CONTAINING TWO TETRAZA MACROCYCLIC LIGANDS AND AN ORGANIC MOLECULE OF HIGH MOLECULAR WEIGHT

7.1. Abstract : Some novel peroxo complexes of molybdenum(VI) and uranium(VI) containing two quardridentate, tetraza-macrocyclic ligands and an organic molecule of high molecular weight have been synthesized and characterized. The complexes have the general formula $[M(O)_2(O_2)\ L]$ M = Mo^{VI} and U^{VI}; L = [15] ane N_4 : 1, 4, 8, 12-tetraazacyclopentadecane and trans-[14]-diene : 5, 7, 7, 12, 14, 14-hexamethyl 1, 4, 8, 11-tetraaza-cyclotetradeca-4, 11-diene) and $[M(O)(O_2)(\text{cyanex-272}^-)_2]$ (cyanex-272$^-$ = bis (2, 4, 4-trimethyl pentyl) (phosphinate). The peroxo complexes containing macrocyclic ligands were found to be inert towards oxidation, but those containing cyanex - 272 were found to oxidize allyl alcohol, trans stilbene and also PPh_3 and $AsPh_3$, to their oxides. The IR spectra of the complexes indicate that the frequency of the ν_1 mode of the $M(O_2)$ grouping, which is essentially an O-O stretch decreases with an increase in the atomic number of the metals in a group.

7.2: EXPERIMENTAL

7.2.1: Preparation of 5, 7, 7, 12, 14, 14, - hexamethyl- 14, 8, 11 - tetraazacyclotetradeca- 4, 11 -diene (trans [14]-diene)[128]

The above macrocycle was prepared as follows: A solution of 1, 2 - diamminoethane (0.15 mol, 10 cm^3) in methanol (100 cm^3) was cooled in an icc bath and conc. HBr (0.32 mol, 34 cm^3) was added dropwise. The white precipitate was filtered off. The product was washed with ether and n-butanol and then dried in *Vacuo* over P_4O_{10}. To the product (1, 2-diamminoethane dehydromide) prepared above (0.02 mol, 4.44 g) was added acetone (100 cm^3) and 1, 2-diammino ethane (0.02 mol, 1.2 gm) The mixture was stirred and heated at 45°C for about an hour, during which time a copious white precipitate of the macrocycle dihydrobromide was formed. The solution was cooled and the product was filtered off, washed with ice cold acetone and ether. It was then dried in *vacuo* over P_4O_{10} mp, 107-108°C.

7.2.2: Preparation of 1, 4, 8, 12 -tetraazacyclo-pentadecane ([15] ane N_4)

The above compound was obtained from Aldrich chemical company and was used as such.

7.2.3. General methods for the preparation of the complex 1 and 2 $[Mo(O)_2(O_2)L]$, (L = [15] ane N_4 or trans [14] -diene)

A suspension of MoO_3 (0.01 mol) in 30% H_2O_2 (50 cm^3) was stirred overnight at 60°C. This was filtered and to the clear filtrate was added a solution of L. (0.01 mol) in ethanol (75 cm^3). The mixture was stirred whilst cooling at the some time in an ice salt bath. A yellow precipitate appeared, which was washed successively with water and ether and dried in *vacuo* over P_4O_{10}.

7.2.4: Preparation of the complex 3 : $[Mo(O)(O_2)(cyanex\text{-}272^-)_2]$ (cyanex-272$^-$ = bis (2, 4, 4-trimethyl pentyl) (phosphinate)

Cyanex-272 (0.01 mol, 2.9 g) was added to a solution of potassium hydroxide(0.01 mol, 0.56 g) in ethanol (80 cm^3). To this clear solution was added, with stirring, a solution of MoO_3 (0.005 mol, 0.72 g) in 30% H_2O_2 (60

cm^3) The mixture was cooled and the resulting precipitate which separated out was filtered, washed with ether and dried in *vacuo* over P_4O_{10}.

7.2.5: General methods for the preparation of the complexes 4 and 5 : $[U(O)_2(O_2)L]$ (L = [15] ane N_4 or trans-[14] -diene)

To a solution of $UO_2(NO_3)_2 \cdot 6\ H_2O$ (0.005 mol) in ethanol (30 cm^3), a solution of L (0.005 mol) in the same solvent (50 cm^3) and then 30% H_2O_2 (30 cm^3) were added. The product was separated and stored as above.

7.2.6: Preparation of 6 : $[U(O)(O_2)(cyanex\text{-}272^-)_2]$

Cyanex-272 (0.004 mol, 1.16 g) was dissolved in a solution of potassium hydroxide (0.004 mol, 0.22 g) in ethanol (50 cm^3). To this solution were added, a solution of $UO_2(NO_3)_2$, 6 H_2O (0.002 mol, 1.04 g) in the same solvent (25 cm^3) and then 30% H_2O_2 (30 cm^3). The product was separated and stored as above.

7.3: REACTIVITIES OF THE COMPLEXES

7.3.1: Reactions of the complexes 1 with allyl alcohol : (A)

Complex 1 was refluxed with allyl alcohol in a 1:1 molar ratio in THF medium for 48 h. It failed to produce any reaction; 1 was recovered unchanged.

7.3.2: Reaction of 4 with trans stilbene : (B)

The complex 4 was refluxed with trans stilbene in a 1:1 molar ratio in CH_2Cl_2 for 24 h. It failed to produce any reaction; 4 was recovered unchanged.

7.3.3: Reaction of 2 and 5 with triphenyl phosphine or arsine : (C)

Refluxing 2 and 5 with equimolar quantities of triphenyl phosphine or triphenyl arsine, respectively, in THF for 48 h also failed to produce any reaction; 2 and 5 were recovered unchanged.

7.3.4: Reaction of 3 with trans-stilbene (D)

Trans-stilbene (0.0086 mol 1.5 g) was added to a suspension of 3 (0.0086 mol, 6.2 g) in CH_2Cl_2 (100 cm^3). The mixture was stirred under reflux for 48h, after which the solution was filtered and TLC indicated a complete conversion of stilbene to its oxide. The filtrate was evaporated and the residue was extracted with ether and evaporation of the extract yielded 1.4 g of trans-stilbene oxide; m.p. 62-64°C (lit m.p., 65-67°C). Anal calc for $C_{14}H_{12}O$: C, 85.71; H, 6.12; O, 8.16. Found C, 85.61, H, 6.10; O, 8.14%.

7.3.5: Catalytic reaction of 3 and H_2O_2 with trans-stilbene (E).

Trans stilbene (0.0086 mol, 1.5 g) was added to 0.08 g of 3 suspended in 60 cm^3 of dioxane and 20 cm^3 of 30% H_2O_2. The mixture was heated under reflux at 90°C for 48 h. It was cooled and filtered and the filtrate evaporated to dryness. The residue was extracted with ether and the extract was dried with Na_2SO_4 and evaporated to dryness. A yellow solid (1.3 g, 87% yield) was identified as benzoin by IR, NMR and mass spectrometry as well as by elemental analysis; m.p. 132-134°C (lit m.p. 134-136°C). Anal calc for $C_{14}H_{12}O_2$ C, 79.24; H, 5.66; O, 15.09. Found C, 79.35; H, 5.64; O, 15.03. No starting material was detected in TLC.

7.3.6: Reaction of 6 with allyl alcohol : (F)

Compound 6 (0.01 mol, 8.6 g) was suspended in 70 cm^3 of THF and a stoichiometric amount of allyl alcohol was added. The mixture was refluxed at 60°C for 24h. Microdistillation under ca 19 mm Hg yielded glycidol [0.45 g, 77% yield] at 147-150°C. The glycidol was identified from its boiling point.

7.3.7: Catalytic reaction of 6 and H_2O_2 with allyl alcohol : (G)

A 20 cm^3 quantity of allyl alcohol (0.294 mol, 17.04 g) was dissolved in 25 cm^3 of dioxane and 0.9 g of 6 was added followed by 20 cm^3 of 30% H_2O_2. The mixture was kept under reflux at 90°C for 24 h. The reaction mixture was filtered and the filtrate distilled at 19 mm Hg pressure. The fraction collected at 178-180°C was identified as glycerol [15 g, 55% yield].

7.3.8: Reaction of 3 with triphenyl phosphine : (H)

A solution of triphenyl phosphine (0.005 mol, 1.3 g) in THF (30 cm^3) was added to suspension of 3 (0.005 mol, 3.6 g) in the same solvent (75 cm^3). The mixture was refluxed for 48 h. The progress of the reaction was monitored by TLC which indicated that the reaction was complete. The solution was filtered and the residue collected. A yellowish white powder was recovered from the filtrate which was identified as $OPPh_3$ [m.p. 156-157°C (lit 157°C)].

7.3.9: Reaction of 6 with triphenyl arsine :(I)

A solution of triphenyl arsine (.005 mol, 1.5 g) in THF (50 cm^3) was added to a suspension of 6 (0.005 mol, 4.3 g) in the same solvent (100 cm^3). The mixture was refluxed for 48 h. TLC indicated that arsine was converted complelety to its oxide. The solution was filtered and the residue collected. Evaporation of the filtrate yielded the product [m.p. 188–189°C (lit 189°C)].

7.4: RESULTS AND DISCUSSION

Elemental analyses and conductivity data for the complexes are presented in Table 10. The molar conductance values show that all of the complexes are non-electrolytes in DMSO indicating that the chelating ligands are all covalently bonded in all the cases. It also supports that the organic molecule cyanex-272 deprotonates at the – OH end providing an oxo coordination, the other coordination site being the oxygen of >P=O group. The complex of cyanex-272 are probably seven-coordinated. The structure of the complex containing macrocyclic ligands, however cannot be postulated without having the single crystal data. Several attempts to develop single crystal failed.

IR spectral data are presented in Table 11. The ligands [15] ane N_4 and trans- [14] -diene are potentially quardridentate co-ordinating via the four ring nitrogens. The free tetraaza-ligands show (ν-H) (Table 11) bands which are shifted to lower frequencies in 1, 2, 4 and 5 indicating that these nitrogens are co-ordinated Further the free trans- [14] -diene exhibits ν(C=N) band at 1670 cm^{-1} which is shifted to lower frequencies in 2 and 5. These are also apparent from the ν(M-N) modes at 260–360 cm^{-1} in the far IR spectra of the complexes[43,55,93-95,112,125,126]. These complexes are the first reported examples of its kind.

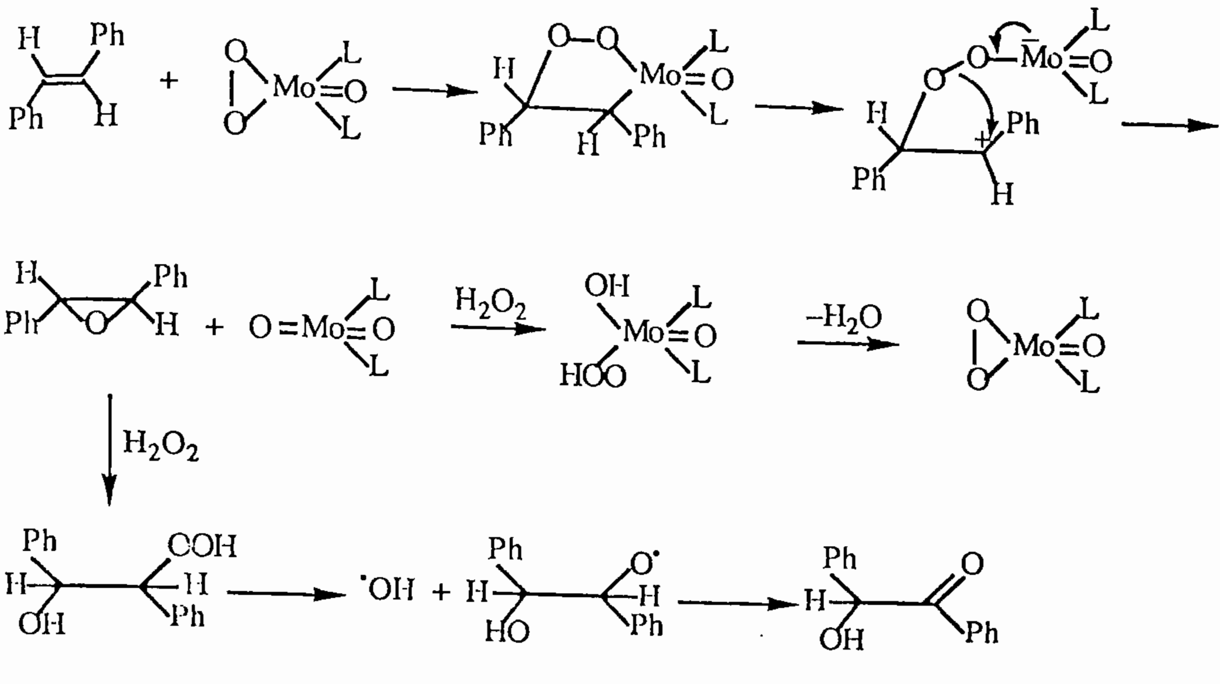
Cyanex-272 is potentially bidentate, coordinating via the >P=O oxygen and the oxo anion generated in basic medium. Attempts to prepare complexes from a neutral medium were unsuccessful. This suggests that the nucleophilicity of the ligand is greatly enhanced in alkaline medium probably due to creation of an anionic site *in situ*. The deprotonation and consequent formation of on anionic site *in situ* is favoured by the basicity of the medium and the ν(OH) band of the free ligand disappear in the spectra of the complexes 3 and 6 thus providing an oxo coordination. That the ligand deprotonates at the - OH end is also evident from the appearance of ν(M-O′) (O′= oxygen in organic ligand) modes at 370–395 (Table 11) in the far IR spectra of the complexes. The ν(P=O) band observed at 1170 cm^{-1} in the free cyanex is shifted to lower frequencies (1055–1060 cm^{-1} in 3 and 6 indicating coordination via oxygen of >P=O group. Complexes 1–6 show diagnostic bands at 885–960 cm^{-1} attributable to ν(M=O) modes [43,98,112]. Complexes 1, 2, 4 and 5 show two bands due to ν(M=O) modes, presumably arising from Cis-orientations of two M=O groups. The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman-active vibrational modes. These are predominantly O–O stretching (ν_1), the symmetric M-O stretch (ν_2) and the antisymmetric M-O stretch (ν_3). The characteristic ν_1(O–O) modes of 1–6 appear at 840–870 cm^{-1} (Table 11). In particular, the ν_1 mode decreases upon passing from molybdenum complexes (1–3) (860–870 cm^{-1}) to the corresponding uranium complexes (4–6) (840–845 cm^{-1}). The present study thus suggests that for the $M(O_2)$ grouping the ν_1(O–O) modes decrease with an increase in the atomic member of metals in a particular group. The present peroxo complexes display ν_3 and ν_2 modes at 645–660 and 510–570 cm^{-1} respectively (Table 11). The complexes 1, 2, 4 and 5 are probably eight coordinated. Eight coordinated peroxo complexes are not rare; Griffith *et al.*[99] reported recently a number of eight-coordinated peroxo complexes of various transition metals.

7.5: REACTIVITY

The peroxo complexes 1, 2, 4 and 5 were inert towards oxidation of olefins, phosphines and arsines. These negative results out line the enhanced stability of the metal peroxo moiety in the presence of quardridentate macrocycles which precludes oxygen transfer reactions. We also observed a similar stabilizing effect of the peroxo complexes containing various multidentate organic ligands[43,93,97,98,112]. However 3 and 6 were reactive and oxidations of trans-stilbene allyl alcohol, phosphine and arsine have been investigated. The various conditions are described in the experimental section.

Reaction D produced trans-stilbene oxide as indicated by a strong IR bands at 1058 cm^{-1} assigned to the C-O-C stretching mode and the ^1H NMR spectrum displayed methine absorption at 3.85 ppm as required for trans-stilbene oxide. Further,the mass spectrum of the product gave a molecular ion peak at m/e 196.

In reaction E 3 was used to catalyze the oxidation of trans-stilbene by H_2O_2 to produce a high yield of the product that however in this case was benzoin. The IR spectrum of the product (KBr pellet) displayed $\nu(C=O)$ at 1685 cm^{-1} and $\nu(O-H)$ at 3385 cm^{-1}. The ^1H NMR spectrum showed methine absorption at 6.0 ppm. The mass spectrum showed a molecular ion peak at m/e 212. A possible reaction path is shown in scheme 8.



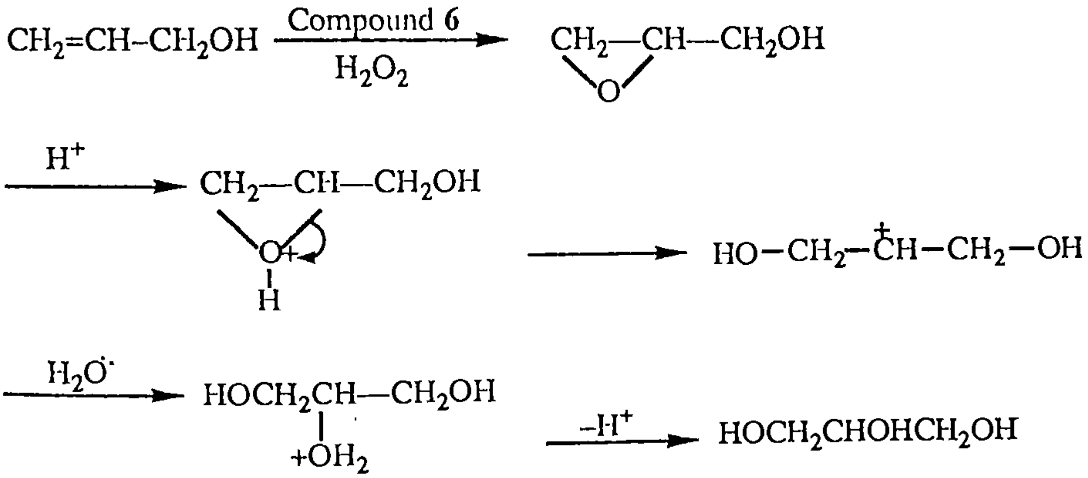
L = deprotonated Cyanex–272

SCHEME 8

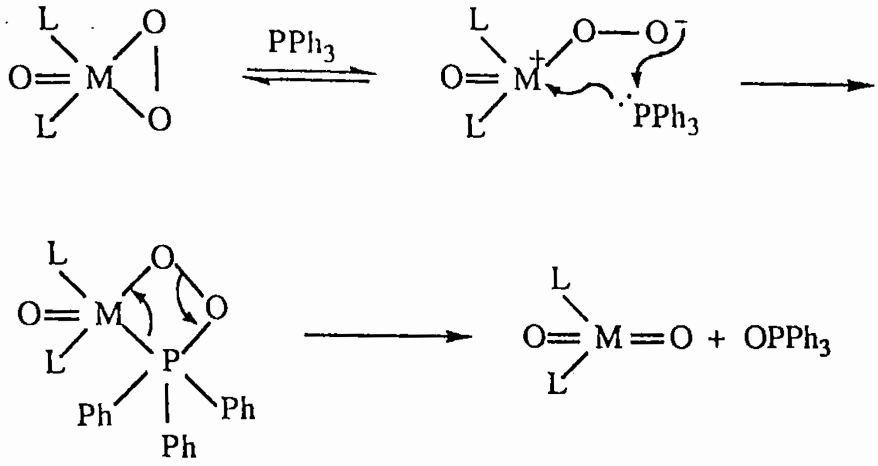
Reaction F produced glycidol as indicated by an IR band at 1060 cm^{-1} assigned to C-O-C stretching mode [40,93,96]. With H_2O_2 and only a catalytic amount of **6** the product isolated was glycerol as indicated by its boiling point. The IR spectrum was identical with that of an authentic sample. Its ^1H NMR spectrum showed methylene and methine absorptions at 3.65 and 5.2 ppm. respectively. A possible reaction path is shown in scheme 9.

Reaction H produced triphenyl phosphine oxide. The IR spectrum of the product showed $\nu(P{=}O)$ at 1192 cm^{-1}, [110]. The IR spectrum of the metal residue left after oxidation showed disappearance of $\nu_1(O{-}O)$ band. Reaction

I with triphenyl arsine produced triphenylarsine oxide as was evident from the IR band at 880 cm^{-1} assigned to $\nu(As=O)$[111]. The IR spectrum of the metal residue showed the disappearance of $\nu_1(O-O)$ band. A possible reaction path is shown in scheme 10. So that additional evidence that the peroxo oxygen is transferred to PPh_3 or $AsPh_3$ could be gained, a blank experiment was performed in the absence of the complex under identical conditions, which failed to give the product. This precludes autoxidation of PPh_3 or $AsPh_3$ under the experimental conditions used. A 30% H_2O_2 solution it self oxidizes PPh_3 or $AsPh_3$ to their oxides which therefore limits the scope of the complexes 3 and 6 to be used as catalysts along with H_2O_2 for the above oxidation.



SCHEME 9



M = Mo^{VI} or U^{VI}; L = deprotonated Cyanex–272.

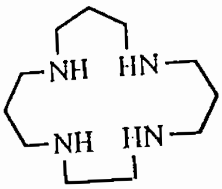
SCHEME 10

Table 10. Analytical data and other physical properties of the peroxo complexes[a].

No. Compound	Colour	% Carbon		% Hydrogen		% Nitrogen		Molar conductance
		calc.	Found	calc.	Found	calc.	Found	(Ω^{-1} cm^2 mol^{-1})
1. $[Mo(O)_2(O_2)[15]ane\ N_4]$	yellow	35.30	35.21	7.00	6.89	14.97	14.85	0
2. $[Mo(O)_2(O_2)trans\text{-}[14]\text{-}Diene]$	yellow	43.64	43.52	7.32	7.31	12.72	12.58	2
3. $[Mo(O)(O_2)(Cyanex\text{-}272^-)_2]$	yellow	53.17	53.10	9.48	9.45			0
4. $[U(O)_2(O_2)[15]ane\ N_4]$	yellow	25.58	25.46	5.07	5.06	10.85	10.78	1
5. $[U(O)_2(O_2)trans\text{-}[14]\text{-}Diene]$	yellow	32.99	32.73	5.54	5.48	9.62	9.54	3
6. $[U(O)(O_2)(Cyanex\text{-}272^-)_2]$	yellow	44.44	44.14	7.93	7.82			0

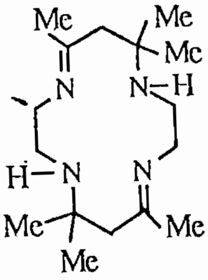
[a]The organic moieties for the compounds are:

[15]ane N_4 =



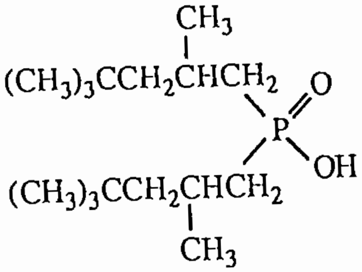
1 „ 4

trans-[14]-diene =



2,5

Cyanex–272 =



3,6

Table 11. IR spectral data for the Mo^{VI} and U^{VI} complexes[a] [band maxima (cm^{-1})].

Compound	ν(O-H)	ν(N-H)	ν(C=N)	ν(P=O)	ν(M=O)	ν_1(O-O)	$\nu_3\left(\mathrm{M}{<}^{O}_{O}\right)$	$\nu_2\left(\mathrm{M}{<}^{O}_{O}\right)$	ν(M-O)	ν(M-N)
[15] ane N_4		3200-3300br								
trans-[14]-Diene		3300br	1670vs							
Cyanex-272	3500-3600br			1170s						
1.		3050-3100br			910vs 920vs	870s	660m	550s		350s
2.		3100br	1625vs		960m 945m	860s	650w	570m		360s
3.				1055s	950s	860s	655m	560w	370s	
4.		3055-3150br			900s 890s	840s	640s	520m		265s
5.		3150br	1620s		900s 885s	840s	645m	510w		260m
6.				1060s	900s	845s	650sh	520m	395s	

[a] Relative band intensities are denoted by vs, s, m, w, br and sh representing very strong, strong, medium, weak, broad and shoulder respectively.

CHAPTER 8

PEROXO COMPLEXES OF Mo(VI), U(VI), Zr(IV) and Th(IV) IONS CONTAINING SOME AMINO ACIDS..

8.1. **Abstract :** Several new peroxo complexes of Mo(VI), U(VI), Zr(IV) and Th(IV) ions containing some bidentate amino acids have been synthesized and characterized. The complexes have the general formula $[M(O)(O_2)L^-_2]$, $[M'(O_2)L^-_2]$, $[M(O)(O_2)L'^{=}H_2O]$ and $[M'(O_2)L'^{=}H_2O]$ [M = Mo(VI) and U(VI); M' = Zr(IV) and Th(IV); L^- = glycinate, leucinate; $L'^{=}$ = tyrosinate]. The complexes were reactive towards trans-stilbene, PPh_3 and $AsPh_3$ giving their oxides. The IR spectra of the complexes indicate that the frequency of the ν_1 mode of the $M(O_2)$ grouping which is essentially an O–O stretch decreases with an increase in the atomic number of metals in a group.

8.2: EXPERIMENTAL

8.2.1: General method for the preparation of 1 and 3, $[Mo(O)(O_2)(L^-)_2]$ and 4 $[Mo(O)(O_2)(L'^{=})$. $H_2O]$ [L = glycine or leucine; L' = tyrosine]:

Preparation of 1 and 3 :

The amino acid L (0.02 mol) was dissolved in ethanol (60 cm^3) and was treated with potassium hydroxide (0.02 mol). The solution was cooled and to it was added, a solution of MoO_3 (0.01 mol) in 30% H_2O_2 (75 cm^3). The mixture was cooled in an ice-salt bath. The resulting precipitate was separated washed with ether and dried in *vacuo* over P_4O_{10}. The complex 4 was prepared similarly using equimolar quantities of tyrosine and MoO_3.

8.2.2: General method for the preparation of 2 and 8 $[U(O)(O_2)(L^-)_2]$ [L = glycine and leucine].

The amino acid L (0.01 mol) was dissolved in a solution of potassium hydroxide (0.01 mol) in 30% H_2O_2 (80 cm^3). The solution was cooled and to it was added a solution of $UO_2(NO_3)_2.6H_2O$ (0.005 mol) in ethanol (60 cm^3). The mixture was cooled in an ice-salt bath. The crystals so obtained were removed by filtration, washed with ether and dried *in vacuo* over P_4O_{10}.

8.2.3: General method for the preparation of 5 and 7, $[M(O_2)L'^{=}.H_2O]$ and 6. $[Th(O_2)L^{-}_2]$ [M = Zr(IV) and Th(IV); L = leucine; L = tyrosine].

The amino acid L or L′(0.01 mol) was added to a solution of potassium hydroxide (0.01 mol) in 30% H_2O_2 (80 cm^3). The solution was cooled and to it was added a solution of stoichiometric amount of $M\ (NO_3)_4.4H_2O$ in ethanol (50 cm^3). The complexes obtained were removed by filtration, washed with ether and dried *in vacuo* over P_4O_{10}.

8.3: REACTIVITIES OF THE COMPLEXES

8.3.1. Reaction of 1 with trans-stilbene (Reaction A)

Trans-Stilbene (1.8 g, 0.01 mol) was added to a suspension of 1 (2.9 g, 0.01 mol) in CH_2Cl_2 (150 cm^3). The mixture was stirred under reflux and the progress of the reaction was monitored by TLC. After 36 h of reflux TLC indicated a complete conversion of stilbene to its oxide. The solution was filtered and the filtrate evaporated and the residue extracted with ether and evaporation of the extract yielded 1.75 g of trans-stilbene oxide, m.p. 63-65°C) (Found: C, 85.55; H, 6:00; O, 8.12. $C_{14}H_{12}O$ calcd.: C,85.71; H, 6,12; O, 8.16%).

8.3.2: Reaction of 2 with trans-stilbene (Reaction B)

Trans-Stilbene(1.4 g, 0.005 mol) was added to a suspension of 2 (2.17 g, 0.005 mol) in CH_2Cl_2 (100 cm^3). The mixture was stirred under reflux and the progress of the reaction was monitored by TLC which after

24 h of reflux indicated a complete conversion of stilbene to its oxide. The solution was filtered and the filtrate evaporated and the residue extracted with ether and the evaporation of the extract yielded 1.35 g of trans-stilbene oxide. The product was characterized from its m.p. and elemental analyses.

8.3.3: Reaction of 6 with triphenylphosphine (Reaction C)

A solution of triphenylphosphine (1.3 g, 0.005 mol) in THF (35 cm^3) was added to a suspension of 6 (2.62 g, 0.005 mol) in the same solvent (80 cm^3). The mixture was refluxed for 24h. The progress of the reaction was monitored by TLC which indicated that the reaction was complete. The solution was filtered and the residue collected. A yellowish white powder was recovered from the filtrate which was identified as $OPPh_3$ [m.p.155-157°C (lit. 157°C)].

8.3.4: Reaction of 8 with triphenylarsine (Reaction D)

A solution of triphenylarsine (1.5 g, 0.005 mol) in THF (60 cm^3) was added to a suspension of 8 (2.73 g, 0.005 mol) in the same solvent (70 cm^3). The mixture was refluxed for 24 h. TLC indicated that arsine was converted completely to its oxide. The solution was filtered and the residue collected. Evaporation of the filtrate yielded the product [m.p.187-188°C (lit, 189°C)].

8.4: RESULTS AND DISCUSSION

Elemental analyses and conductivity data for the complexes are presented in Table 12. The complexes are all non-electrolytes in solution suggesting that the anions are covalently bonded in all the cases. These data are consistent with seven-fold coordination of molybdenum(VI) and uranium(VI) complexes, while the zirconium(IV) and thorium(IV) analogues are hexa-coordinated.

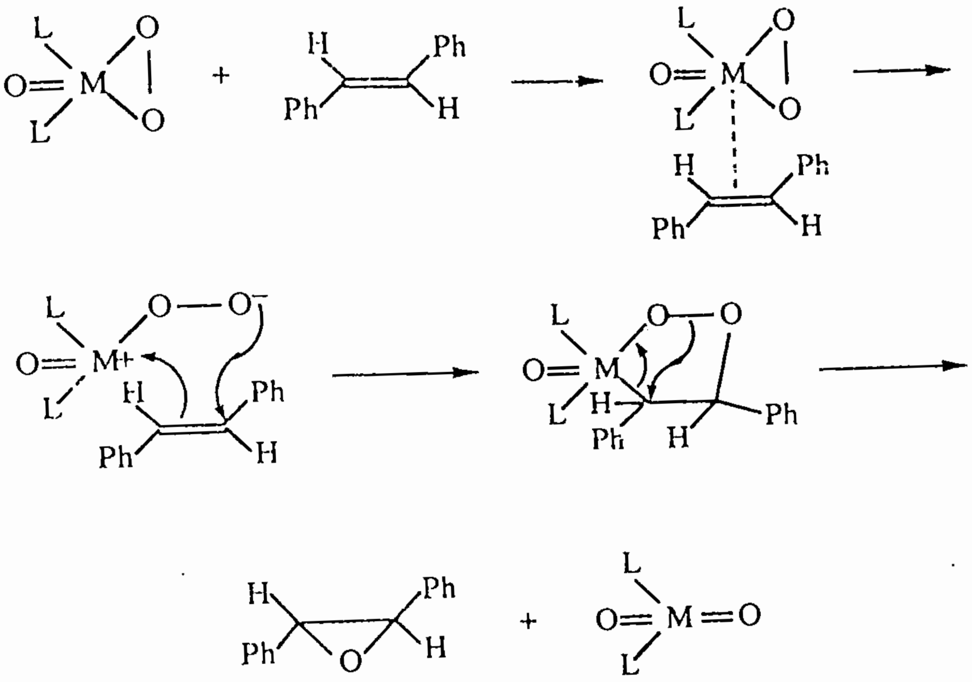
IR spectral data are presented in Table 13. In alkaline medium the amino acids glycine and leucine behave as bidentate ligands coordinating via the amino nitrogen and the carboxylate anions. Tyrosine is , however, potentially tridentate, coordinating via the amino nitrogen, carboxylate anion and the oxo anion generated during complexation. This is also apparent from the non-electrolytic nature of the complexes. In addition, absence of band in the region 3400-3600 cm^{-1} in the spectra of the complexes of tyrosine indicate that it undergoes deprotonation at the OH end, thus providing an oxo coordination. All of the complexes have characteristic $\nu(NH_2)$ stretching modes in the region 3075-3195 cm^{-1}, indicating coordination by the amino nitrogen. This is also evident from the appearance of bands at 275-375 cm^{-1} (Table 13) which are tentatively attributed to the ν(M-N) mode[43,55,93-99,112] (M = Zr^{IV}, Th^{IV}, Mo^{VI} and U^{VI}). Complexes 1-8 display ν(C=O) bands at 1640-1670 cm^{-1}, characteristic of carboxylate binding in the complexes[43,93,112]. This is also evident from the appearance of ν(M-O′) (O′= oxygen in organic ligands) modes at 390-430 cm^{-1} in the far IR spectra of the complexes[43,55,93-99,112]. Complexes 1-4 and 8 show diagnostic bands at 910-925 cm^{-1}, attributable to ν(M=O) modes[43,94-98,112]. The metal peroxo grouping (local C_{2v} Symmetry) gives rise to three IR and Raman-active vibrational modes. These are predominantly O-O stretching (ν_1), the symmetric M-O stretch (ν_2) and the antisymmetric M-O stretch (ν_3). The characteristic ν_1(O-O) modes of 1-8 appear at 815-870 cm^{-1} (Table 13). In particular, the ν_1 mode decreases upon passing from molybdenum complexes (1, 3 and 4) (865, 870 and 860 cm^{-1}) to the corresponding uranium complexes (2 and 8) (840 and 835 cm^{-1}). Again, in the case of peroxo complexes of the elements of group 4A, there is a decrease in ν_1 upon passing from the zirconium complex (5) (830 cm^{-1}) to the thorium complexes (6 and 7) (815 and 820 cm^{-1}). The present study thus clearly revels that for the $M(O_2)$ grouping, the ν_1(O-O) modes decrease with an increase in the atomic number of metals in a particular group. The present peroxo complexes display ν_3 and ν_2 modes at 625-670 and 505-570 cm^{-1}, respectively (Table 13).

8.5: REACTIVITY

To explore the reactivity of the present peroxo complexes, 1 and 2 were allowed to react with trans-stilbene while 6 and 8 were used to oxidize triphenylphosphine and triphenylarsine, respectively.

Reactions A and B produced trans-stilbene oxide as indicated by a strong IR band near 1060 cm^{-1} assigned to the C-O-C stretching mode and the ^1H NMR spectra displayed methine absorption at 3.8 ppm as required for trans-stilbene oxide. The mass spectra indicated molecular ion peak at m/e^+ 196. Experimental details indicated that Reaction B was faster than Reaction A, indicating that the uranium peroxo complex was kinetically more labile than its molybdenum analogue. A possible reaction path is shown is Scheme 11.

Reaction C produced triphenylphosphine oxide. The IR spectrum of the product showed ν(P=O) at 1190 cm^{-1} [110]. Reaction D, with triphenylarsine, produced triphenylarsine oxide, as was evident from the IR band at 880 cm^{-1} assigned to ν(As=O)[111]. The IR spectra of the metal residues of reactions C and D showed the disappearance of ν_1(O-O) bands. A possible reaction path is shown in Scheme 12. So that additional evidence that the peroxo oxygen is transferred to PPh_3 or As Ph_3 could be gained, a blank experiment was performed in the absence of the complex under identical conditions, which failed to give the product.



$M = Mo^{VI}$ and U^{VI}; $L = NH_2CH_2COO^-$

SCHEME 11

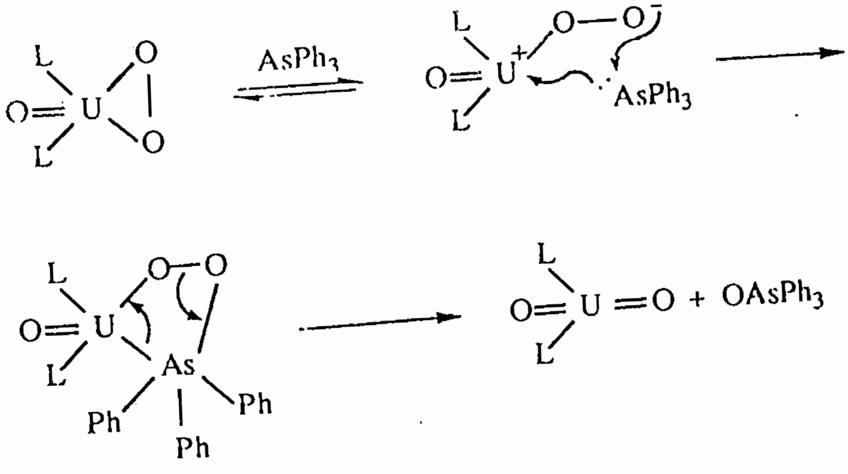


Table 12. Analytical and molar conductance data for the complexes.

No. Complex	Found (Calcd.)%			Molar conductance ohm^{-1} cm^2 mol^{-1}
	C	H	N	
1. $[Mo(O)(O_2)(NH_2CH_2COO^-)_2]$	16.41 (16.45)	2.71 (2.76)	9.48 (9.56)	0
2. $[U(O)(O_2)(NH_2CH_2COO^-)_2]$	11.00 (11.01)	1.85 (1.86)	6.41 (6.45)	2
3. $[Mo(O)(O_2)(C_2H_5CH(CH_3)CH(NH_2)COO^-)_2]$	35.61 (35.65)	5.78 (5.98)	6.89 (6.93)	4
4. $[Mo(O)(O_2)(^-OC_6H_4CH_2CH(NH_2)COO^-)H_2O]$	31.45 (31.69)	3.11 (3.25)	4.10 (4.11)	1
5. $[Zr(O_2)(^-OC_6H_4CH_2CH(NH_2)COO^-).H_2O]$	33.70 (33.74)	3.43 (3.46)	4.34 (4.37)	0
6. $[Th(O_2)(C_2H_5CH(CH_3)CH(NH_2)COO^-)_2]$	27.45 (27.49)	4.52 (4.61)	5.22 (5.34)	0
7. $[Th(O_2)(^-OC_6H_4CH_2CH(NH_2)COO^-)H_2O]$	23.23 (23.44)	2.40 (2.40)	3.00 3.04	1
8. $[U(O)(O_2)(C_2H_5CH(CH_3)CH(NH_2)COO^-)_2]$	26.21 (26.38)	4.24 4.43	5.11 5.13	2

Table 13. Infrared spectral data for the complexes [band maxima (cm^{-1}) [band maxima (cm^{-1})]^{a}

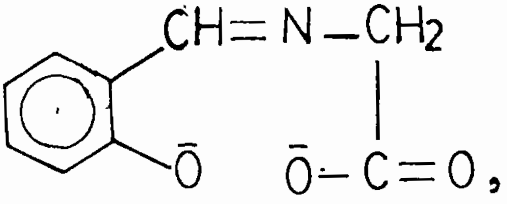
No. Compound	ν(O-H)	ν(NH$_2$)	ν(C=O)	ν(M=O)	ν_1(O-O)	$\nu_3(\mathrm{M}\begin{smallmatrix}\mathrm{O}\\ \vert\\ \mathrm{O}\end{smallmatrix})$	$\nu_2(\mathrm{M}\begin{smallmatrix}\mathrm{O}\\ \vert\\ \mathrm{O}\end{smallmatrix})$	ν(M-O′)	ν(M-N)
1.		3195m 3105m	1650s	920vs	865s	630s	510m	405m	360sh
2.		3200w 3110m	1665s	910vs	840s	625m	505s	400w	270s
3.		3180m 3095w	1655vs	925vs	870vs	635s	525m	410sh	370m
4.	3090br	3185m 3075m	1660s	920vs	860s	635m	520m	415w	375w
5.	3400br	3180m 3075w	1640vs		830s	670m	560m	430sh	325m
6.		3195m 3090m	1650s		815vs	660m	570s	395m	305w
7.	3410br	3190m 3095m	1655vs		820s	655sh	540s	390m	310w
8.		3210w 3115m	1670s	915vs	835s	635vs	515m	405m	275m

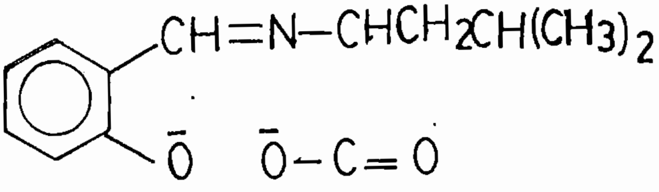
[a] Relative band intensities are denoted by vs, s, m, w br and sh representing very strong, strong, medium, weak, broad and shoulder respectively.

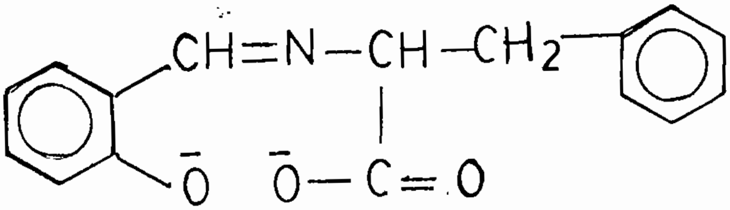
CHAPTER 9

PEROXO COMPLEXES OF Mo(VI), W(VI), U(VI), Zr(IV) and Th(IV) IONS CONTAINING TRIDENTATE SCHIFF BASES DERIVED FROM SALICYLALDEHYDE AND AMINO ACIDS.

9.1: Abstract : New organoperoxo complexes of molybdenum(VI), tungsten(VI), uranium(VI), zirconium(IV) and thorium(IV) ions containing tridentate schiff bases formed by the condensation of an amino acid (glycine, leucine or phenyl alanine) and salicylaldehyde have been synthesized and characterized. The complexes have the general formula $[M(O)(O_2)L]$ M = Mo(VI), W(VI) or U(VI) and $[M'(O_2)L.H_2O]$, [M' = Zr(IV) or Th(IV). and L = a dinegative schiff base]







These peroxo complexes were found to be inert towards oxidation. The size of the metals influences the mode of coordination of the peroxo moiety. The frequency of the ν_1 mode of the $M(O_2)$ grouping which is essentially and O-O stretch, decreases with an increase in the atomic number of the metals in a particular group.

9.2: EXPERIMENTAL

9.2.1: Preparation of the schiff bases :

An amino acid (glycine, leucine or phenyl alanine) (0.01 mol] together with 0.01 mole of potassium hydroxide in 60 cm^3 of water was stirred for an hour at 50-60°C to get a clear solution. A solution of salicylaldehyde (0.01 mol) in ethanol (20 cm^3) was added to it and the mixture was heated for 2-3 hour at 50-60°C when a clear yellow solution was obtained. Several attempts to solidify the schiff bases failed. Therefore the schiff bases were used *in situ* [132-133] for the syntheses of the peroxo complexes.

9.2.2: General method for the preparation of complexes (1, 2, 6, 7, 11 and 12; $[M(O)(O_2)L]$ [M = Mo(VI) or W(VI)., L = a dinegative schiff base.]

A suspension of MO_3 (0.01 mol) in 30% H_20_2 (60 cm^3) was stirred over night at 45-50°C to get a clear solution. This was cooled and to the cold solution was added a solution of the previously prepared schiff bases. The precipitate appeared was filtered, washed successively with water and ether and then dried *in vacuo* over P_4O_{10}

9.2.3: General method for the preparation of the complexes (3, 8 and 13). $[U(O)(O_2)\ L]$.

To a cold solution of $UO_2\ (NO_3)_2 \cdot 6H_20$ (0.01 mol) in ethanol (50 cm^3) was added successively the previously prepared cold solution of the schiff bases and 30% H_2O_2 (30 cm3). The yellow precipitate formed was filtered, washed with water and ether and dried *in vacuo* over P_4O_{10}.

9.2.4: General method for the preparation of complexes (4, 5, 9, 10, 14, and 15) $[M(O_2)L.\ H_2O]$ $[M = Zr(IV)$ or $Th(IV)]$.

$M(NO_3)_4$, $4H_2O$ (0.01 mol) in water (30 cm^3) was added to a cold solution of the previously prepared schiff base followed by the addition of 40 cm^3 of 30% H_2O_2. The mixture was cooled in ice. The precipitate appeared was filtered, washed with water and ether and then stored as before.

9.3: REACTIVITIES OF THE COMPLEXES :

9.3.1: Reaction of 1, 4 or 7 with allyl alcohol.

Refluxing of 1 or 4 with allyl alcohol in a 1:1 molar ratio in tetrahydrofuran (THF) medium for 48h. failed to produce any reaction; 1 and 4 were recovered unchanged.

Refluxing of 7 with allyl alcohol in the presence of a large excess of 30% H_2O_2 in dioxane medium for 48h. at 90°C also failed to produce any reaction; 7 was recovered unchanged.

9.3.2: Reactions of 10 or 14 with triphenyl phosphine.

Refluxing of 10 and 14 with equimolar quantities of triphenyl phosphine in THF for 48h. failed to produce any reaction. 10 and 14 were recovered unchanged.

9.3.3: Reactions of 3, 5 or 8 with triphenyl arsine.

Refluxing 3, 5 or 8 with equimolar quantities of triphenyl arsine in THF for 48h. also failed to produce any reaction 3, 5 and 8 were recovered unchanged.

9.4: RESULTS AND DISCUSSION

Elemental analyses and conductivity data of the complexes (1-15) are presented in Table 14. The molar conductance values show that all of the complexes are non-electrolytes in DMSO indicating that the chelate anions are covalently bonded in all the cases. These data are consistent with six fold coordination of the metal complexes.

IR spectral data are presented in Table 15. All the schiff bases are potentially tridentate, coordinating at the imino nitrogen and two oxygen atoms[43]. In the complexes the appearance ofν(C=N) band at (1550-1600) cm^{-1} indicates coordination through the imino nitrogen atoms[107]. This is also evident from the ν(M-N) mode at (270-360) $cm^{-}1$ in the far IR spectra of the complexes[43,55,71,94,122,123].

The ν(OH) bands of the free ligand in the region 3400-5500 cm^{-1} disappear in the complexes 1, 2, 3, 6, 7, 8, 11, 12 and 13 which indicate deprotonaion at the -OH end. thus providing oxo coordination. That the ligands deprotonate at the -OH end is also evident from the appearance of ν (M-O′) modes, (O′=oxygen in organic ligand) at (370-420) cm^{-1} (Table 15.) in the far IR spectra of the complexes[43,55,71,93,94,96]. All the complexes display ν (C=O) modes at (1625-1650)cm^{-1} characteristic of carboxylate binding in the complexes. The complexes (1-3, 6-8, 11-13) show diagnostic bands at (905-940) cm^{-1} attributable to ν(M=O) modes[43,93,94,96]. The complexes (4, 5, 9, 10, 14 and 15) show broad bands at (3400-3500)cm^{-1} due to coordinated water molecules. The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman active vibrational modes. These are predominately O-O stretch (ν_1), the symmetric M-O stretch (ν_2) and antisymmetric M-O stretch (ν_3). The characteristic ν_1(O-O) modes of the complexes (1-15) appeared at (815-890) cm^{-1} (Table 15.). In particular the ν_1 mode decreases upon passing from molybdenum complexes (1, 6 and 7) to the corresponding tungsten complexes (2, 6 and 12) which then further decreases for uranium complexes (3, 8 and 13) (Table 15) Besides in the case of the peroxo complexes of the elements of group 4A, there is decrease in ν_1 mode upon passing from Zirconium complex (4, 9 and 14) to the corresponding thorium complexes (5, 10 and 15). The present study thus clearly reveals that for the M(O_2) grouping the ν_1(O-O) modes decrease with an increase in the atomic number of the metals in a particular group. The present peroxo complexes display ν_3 and ν_2 modes at (615-690) cm^{-1} and (520-570) cm^{-1} respectively.

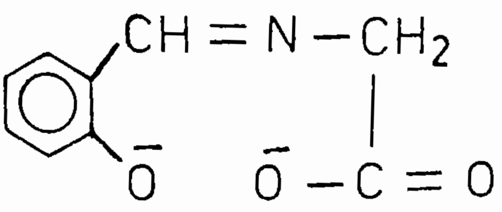
9.5: REACTIVITY :

The peroxo complexes of molybdenum, tungsten, uranium, zirconium and thorium were not explosive. So that the possible reactivity of the present peroxo complexes toward olefinic compounds could be explored. The present peroxo complexes were all found to be inert towards oxidation of olefin and other substrates, triphenyl phosphine or triphenyl arsine. These negative results out line the enhanced stability of the metal-peroxo moiety in the presence of tridentate dinegative chelating ligand, which precludes oxygen transfer reactions. We also observed a similar stabilizing effect of the peroxo complexes containing various multidentate ligand[43,55,71,98].

Table 14. Analytical data and other physical properties of the complexes[a].

	Colour	% Metal		% Carbon		% Hydrogen		% Nitrogen		Molar conductance $\Omega^{-1}cm^{2}mol^{-1}$
		Calc.	Found	Calc.	Found	calc.	Found	calc.	Found	
1. $[Mo(O)(O_2)(C_9H_7NO_3)]$	Yellow	29.9	29.8	33.6	33.8	2.2	2.2	4.4	4.3	0
2. $[W(O)(O_2)(C_9H_7NO_3)]$	Ash	45.0	44.9	26.4	26.3	1.7	1.7	3.4	3.4	0
3. $[U(O)(O_2)(C_9H_7NO_3)]$	Yellow	51.4	51.5	23.3	23.5	1.5	1.4	3.0	3.1	1.5
4. $[Zr(O_2)(C_9H_7NO_3).H_2O]$	Ash	28.6	28.4	34.0	34.1	2.8	2.9	4.4	4.3	1
5. $[Th(O_2)(C_9H_7NO_3).H_2O]$	Ash	50.5	50.2	23.5	23.3	2.0	2.1	3.1	3.2	0
6. $[Mo(O)(O_2)(C_{13}H_{15}NO_3)]$	Yellow	25.5	25.7	41.4	41.2	4.0	4.1	3.7	3.7	1
7. $[W(O)(O_2)(C_{13}H_{15}NO_3)]$	Brown	39.6	39.5	33.6	33.5	3.2	3.3	3.0	3.0	0
8. $[U(O)(O_2)(C_{13}H_{15}NO_3)]$	Yellow	45.9	46.0	30.0	30.1	2.9	3.0	2.7	2.6	2
9. $[Zr(O_2)(C_{13}H_{15}NO_3).H_2O]$	Black	26.2	26.0	45.0	45.3	4.9	5.0	4.0	4.1	1
10. $[Th(O_2)(C_{13}H_{15}NO_3).H_2O]$	Ash	64.6	64.3	43.5	43.3	4.7	4.5	3.9	3.7	2
11. $[Mo(O)(O_2)(C_{16}H_{13}NO_3)]$	Yellow	23.4	23.5	46.7	46.5	3.2	3.3	3.4	3.5	1
12. $[W(O)(O_2)(C_{16}H_{13}NO_3)]$	Ash	36.9	36.7	38.5	38.2	2.6	2.7	2.8	2.9	0
13. $[U(O)(O_2)(C_{16}H_{13}NO_3)]$	Yellow	43.0	42.8	34.7	34.5	2.4	2.5	2.5	2.5	2
14. $[Zr(O_2)(C_{16}H_{13}NO_3).H_2O]$	Ash	22.3	22.1	47.1	47.3	3.7	3.8	3.4	3.5	1
15. $[Th(O_2)(C_{16}H_{13}NO_3).H_2O]$	Brown	42.3	42.1	35.0	35.2	2.7	2.8	2.6	2.6	2

[a]The organic moieties for the complexes are:



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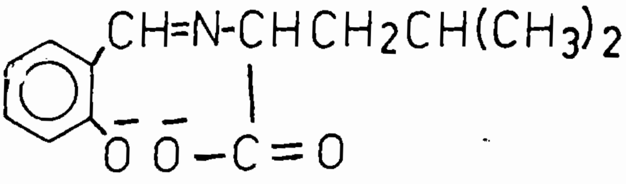


6 — 10

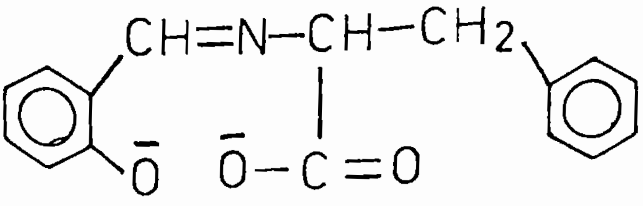


Table 15. IR spectral data for the complexes[a] [band maxima (cm^{-1})].

No. Compound	ν(O-H)	ν(C=O)	ν(C=N)	ν(M=O)	ν_1(O-O)	$\nu_3(\mathrm{M}\langle^{O}_{O})$	$\nu_2(\mathrm{M}\langle^{O}_{O})$	ν(M-O′)	ν(M-N)
1.		1640s	1600s	905s	870s	670s	535s	370s	340s
2.		1650s	1550s	930vs	830vs	640s	525s	380m	315s
3.		1645s	1570s	910vs	815vs	620m	520w	400s	270m
4.	3400-3500br	1650w	1600w		860vs	665s	570m	370s	360s
5.	3300-3500br	1650sh	1600s		820s	675m	570w	400w	350s
6.		1645s	1595s	940s	890s	655m	535s	400w	350s
7.		1645s	1550s	925s	880m	635s	530s	410s	340m
8.		1645s	1560s	915m	860s	625s	520s	400s	295w
9.	3200-3500br	1640s	1580w		865s	660s	580s	410w	360s
10.	3300-3500br	1630br	1600s		830s	650w	570w	405m	325w
11.		1640s	1600s	910s	850s	680s	560m	400s	350s
12.		1645s	1570s	920m	830s	650s	540s	400s	340s
13.		1640s	1580w	905s	820s	630m	520s	415s	320m
14.	3100-3500br	1660s	1580s		840s	690vs	570s	420w	350s
15.	3200-3500br	1640s	1585sh		830m	665s	530s	420w	320w

[a] Relative band intensities are denoded by vs, s, m, w and br representing very strong, strong, medium weak broad and shoulder respectively.

CHAPTER 10

COMPARATIVE REACTIVITIES OF THE PEROXO COMPLEXES OF Mo(VI), U(VI), Zr(IV) and Th(IV) IONS.

10.1: **Abstract :** The reactivities of the peroxo complexes of Mo(VI), U(VI), Zr(IV) and Th(IV) ions towards PPh_3 and $AsPh_3$ were compared on the basis of different sizes of the metals, multidentate nature of the co-ligands and also on the donicity of the ancillary ligands used. It has been observed that the reactivity increases with he increase in the atomic number of the metal in a particular group. The reactivity also depends on the nature of the co-ligands. Peroxo complexes containing mono-dentate ligands were highly reactive than bidentate ligands; compounds containing tridentate or quardridentate ligands were found to be inactive.

10.2: EXPERIMENTAL

10.2.1: Preparation of the complex 1, $U(O)(O_2)_2 \cdot 2OPPh_3$.

$UO_2(NO_2)_2 \cdot 6H_2O$ (0.005 mol) in water (30 cm^3) was added a solution triphenyl phosphine oxide (0.01 mol) in ethanol (30 cm^3). To the mixture was added H_2O_2 (30%) (30 cm^3). The yellow precipitate formed was filtered, washed with ethanol and ether and then dried over P_4O_{10}.

10.2.2: Preparation of the complex 2, $U(O)(O_2)_2 \cdot 2OAsPh_3$.

The same procedure was applied to $UO_2(NO_3)_2 \cdot 6H_{2O}$ (0.005 mol), triphenyl arsine oxide (0.01 mol) and H_2O_2 (30%) (30 cm^3). The precipitate was separated and stored as above.

10.2.3: General method for the preparation of the complexes 3, 4 and 6 $[M(O_2)_2 L]$ and $[U(O)(O_2)_2L]$. [M = Zr(IV) or Th (IV), L = $C_5H_4NNH_2$].

$M(NO_3)_4 4H_2O$ (0.005 mol) or $UO_2(NO_3)_2$. $6H_{20}$ (0.005 mol) in water (30 cm_3) was added a solution of the ligand (0.005 mol) in ethanol (30 cm^3). To the mixture 30% H_2O_2 (30 cm^3) was added immediately with stirring. The precipitate obtained was filtered, washed with ethanol and then dried in vacuo over P_4O_{10}.

10.2.4: Preparation of the complex 5 $[Mo(O)(O_2)_2\ C_5H_4NNH_2]$.

A suspension of MoO_3 (0.005 mol) in 30% H_2O_2 (60 cm^3) was stirred over night at 60°C. This was filtered and to the clear filtrate was added a solution of the ligand, $C_5H_4NNH_2$ (0.005 mol) in ethanol (50 cm^3). The mixture was stirred whilst cooling at the same time in an ice-salt bath. The yellow precipitate formed was filtered, washed with ethanol and ether and then stored as above.

10.2.5: Preparation of the complex 7 $[U(O)(O_2)_2\ det]$.

$UO_2(No_3)_2$. $6H_{20}$ (0.005 mol) in water (30 cm^3) was added a solution of the ligand (0.005 mol) in ethanol (30 cm^3). To the mixture was added H_2O_2 (30%) (30 cm^3) with stirring. The yellow precipitate formed was filtered washed with ethanol and ether and then dried over P_4O_{10}.

10.3: REACTIVITIES OF THE COMPLEXES

10.3.1: Reactivity depending on the size of the metal.

In order to accomplish this complexes 3, 4, 5 or 6 were allowed to react with triphenyl phosphine or arsine. A solution of triphenyl phosphine or arsine in THF (30 cm^3) was added to a suspension of 3 in the same solvent (60 cm^3). Refluxing the mixture for 48h produced phosphine oxide or arsine oxide, the completion of the reaction was monitored by TLC. The same reaction was carried out with 4, 5 or 6 as oxidants and the reactions were found to be completed in 8h, 48h, and 8h respectively.

10.3.2: Reactivity depending on the multidentate nature of the co–ligands.

To examine the reactivity of the peroxo complexes containing mono, bi, and tridentate organic ligands, the complexes 1, 6 or 7 were allowed to react with triphenyl phosphine or arsine. Refluxing the mixture of triphenyl phosphine or arsine and the complexes in THF gave triphenyl phosphine oxide or arsine oxide in 6h with complex 1 and in 8h with complex 6. No phosphine oxide or arsine oxide was formed with complex 7 even when refluxing was continued to 72h.

10.3.3: Reactivity depending on the donicity of the ancillary ligands.

In order to perform this the complexes 1 or 2 were refluxed with triphenyl phosphine or arsine in THF. It has been observed that the phosphine or arsine was completely converted to phosphine oxide or arsine oxide in 6h with complex 1 and in 4h with complex 2 which was monitored by TLC.

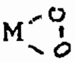
10.4: RESULTS AND DISCUSSION.

The analytical and conductivity data are given in (Table 16). The complexes were all non electrolytes in DMSO suggesting that the complexes were undissociated in solution.

IR spectra data are presented in (Table 17). The characteristic ν_1 (O–O) modes of the complexes appear at (800–850 cm^{-1}) (Table 17). In particular, the ν_1 mode decreases upon passing from zirconium complexes to thorium complexes. The $\nu_1$mode of the uranium peroxo complexes occur at lower frequencies than that of molybdenum and tungsten complexes (Table 17) reported carrier[125].

Thus $\nu_1$mode decreases with the increase of the atomic number of metals in a particular group[93,94,96,125]. More importantly, the $\nu_1$mode of the peroxo complexes containing bidentate and tridentate ligands occur at lower frequencies than those containing mono dentate co-ligands. This is presumably due to the greater charge neutralization of the metal centres by the multidentate δ-donor ligands causing a weaker coulombic interaction in the $M^{n+}-O_2^{2}$ moiety (n=4 or 6).

Complexes 1–6 were found to oxidize phosphines and arsines to their oxides. It is interesting however, that the thorium and uranium peroxo complexes were more reactive than the lighter zirconium or molybdenum analogues. This is perhaps expected that with the increase of size the kinetic instability of metals increases thereby enhancing the nucleophilicity of substrates for an attack.

The insertion of phosphine and arsines into the metal peroxide bond forming a peroxo metallocycle is a concerted process.[42,54] which is very facile for heavier metals. The products $OPPh_3$ and $OAsPh_3$ were characterized from the melting points and IR spectra. The uranium peroxo complex 7 containing a tridentate Co-ligands was however, inert towards triphenyl phosphines or arsines. This findings contradicts the information that the total electronic effect of the multidentate ligands on the metal centre weakens the  bonding (Table 17) which should render stronger oxidizing character to 7 than those containing monodentate ligands. We believe that the positive gain in entropy while using multidentate ligands predominates the electronic effect thereby giving a huge kinetic stability to the metal peroxo moiety in 7.

Westland *et al.*[41] reported that the O-O stretching frequency in peroxo complexes of Mo and W is decreased by replacing a given ligand by one which is a stronger donor. They suggested that the peroxide modes depend on the degree of ionic character in the M-O bonds and this may in turn be affected by the other ligands in the molecule. Griffith has noted that when fluorine replaces a less electronegative element bonded to the central atom of a peroxo complex, the (O-O) stretching frequency is increased[109]. The analogous phosphorus and arsenic-containing ligands (eg $OPPh_3$ and $OAsPh_3$) are spatially very much alike while the pauling elecleonegativities of phosphorus and arsenic are 2.19 and 2.18 respectively-practically identical[130]. Nevertheless, the frequency of the $\nu_1$mode is lower in the arsenic compounds than in the phosphorus analogues. The polarity or the polarizibility of the bond from the group 5A element to oxygen should influence charge displacement toward the metal atom. Reynold and Meek reported the following bond moments for Ph_3EO (E=p or As): P-O, 3.27; As-O 4.77 D. The derived charge separations in the E-O bonds show that the oxygen in the arsine oxide is more negative, and values of $2.45x10^{-10}$ and $1.78x10^{-10}$ e.s.u. were obtained for arsine oxide and phosphine oxide respectively, using 0.74, 1.10 and 1.21 A° as the covalent radii for oxygen, phosphorus and arsenic respectively. The following p^{ka} values were obtained[131] for the protonated oxides; R'_3PO, 9.72; R_3PO, 8.54; R_3AsO, 16.14 (R′ = cyclooctyl, R′ = n-butyl). This evidence again points to a greater polarity in the case of arsine oxides and hence = As-O is a stronger donor than = P-O. This argument seems to apply again in accounting for the lower $\nu_1$value observed for compound 2 compared to 1.

The infrared data also reflects on the reactivity of the complexes. In particular $U(O)(O_2)_2.2\ OAsPh_3$ was more reactive than $U(O)(O_2)_2\ 2OPPh_3$ (see experimental section) toward PPh_3 and $AsPh_3$. This example gives some assurance in the variation of reactivities with respect to the donicity of the co-ligands used in dioxygen complexes.

Table 16. Analytical data and other physical properties of Zr(IV), Th(IV), Mo(VI) and U(VI) peroxo complexes[a].

No.	Compound	Colour	% carbon		% hydrogen		% nitrogen		Molar conductance $ohm^{-1}cm^2mol^{-1}$
			calc.	found	calc.	found	calc.	found	
1.	$[U(O)(O_2)_2.2OPPH_3]$	Yellow	49.4	49.5	3.4	3.5			2
2.	$[U(O)(O_2)_2.2OAsPh_3]$	Yellow	44.9	45.0	3.1	3.2			2
3.	$[Zr(O_2)_2(C_5H_4NNH_2)]$	Brown	24.0	24.1	2.4	2.3	11.2	11.3	1
4.	$[Th(O_2)_2(C_5H_4NNH_2)]$	Colourless	15.4	15.3	1.5	1.5	7.1	7.2	0
5.	$[Mo(O)(O_2)_2(C_5H_4NNH_2)]$	Yellow	22.2	22.1	2.2	2.2	10.3	10.4	2
6.	$[U(O)(O_2)_2(C_5H_4NNH_2)]$	Yellow	14.6	14.5	1.5	1.5	6.8	6.7	0
7.	$[U(O)_2(O_2)$ det]	Yellow	11.9	11.7	3.2	3.2	10.4	10.3	2

Table 17. IR spectral data for Zr(IV), Th(IV), Mo(VI) and U(VI) complexes[a] [band maxima (cm^{-1})].

No. compound	$\nu(NH_2)$	$\nu(C{=}N)$	$\nu(M{=}O)$	$\nu_1(O{-}O)$	$\nu_3(\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{O}})$	$\nu_2(\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{O}})$	$\nu(M{-}N)$
1.			922vs	830s	685m	606m	
2.			907vs	820vs	670m	612m	
3.	3302w 3245w	1600s		840s	680s	590m	385w
4.	3285w 3175w	1570w		830s	600w	525w	310sh
5.	3210w 3100w	1640s		850s	680s	580m	310w
6.	3240m 3100sh	1650w	905vs	810w	600sh	520w	250s
7.	3280w 3180w		900vs	800s	650m	530m	295m

[a] Relative band intensities are denoted by vs, s, m, w, br and sh representing very strong, strong, medium, weak, broad and shoulder respectively.

CONCLUSION.

From the observation obtained in the previous sections, the following conclusions were made.

(1) Peroxo complexes of different metal ions can be used as specific reagents for oxidations of olefinic compounds and triphenyl phosphine or triphenyl arsine.

(2) Peroxo complexes of Zr(IV) Th(IV) Mo(VI) W(VI) and U(VI) ions containing bi dentate uninegative or bidentate neutral ligands are effective oxidizing agents towards oxidation of olefinic compounds, triphenyl phosphine and triphenyl arsine.

(3) Peroxo complexes of Zr(IV), Th(IV) Mo(VI) W(VI) and U(VI) ions containing bidentate dinegative ligands are inactive towards oxidation of ethylenic compounds or PPh_3 or $AsPh_3$. The negative results outline the enhanced stability of the metal peroxo moiety in the presence of bidentate-dinegative chelating ligands.

(4) Peroxo complexes of the above mentioned metal ions containing tridentate or quardridentate ligands are inactive towards oxidation of olefinic compounds and PPh_3 or $AsPh_3$. These negative results outline the enhanced stability of the metal peroxo moiety in the presence of the quardridentate chelating lignds which precludes oxygen transfer reactions.

(5) During the oxidation of ethylenic compounds, PPh_3 or $AsPh_3$ by the peroxo complexes, the peroxo oxygen is transferred to the substrates. This is evident from the disappearance of ν_1 (O–O) bands in the metal residues left after oxidation.

(6) The metal peroxo grouping (local C_{2v} symmetry) gives rise to three IR and Raman - active vibrational modes. These are predominantly (O-O) stretching (ν_1) the symmetric M-O stretch (ν_2) and the antisymmetric M-O stretch (ν_3). In particular the ν_1 mode of the thorium peroxo complexes occur at slightly lower frequencies than the zirconium analogues. This is more discernible in the peroxo complexes of the elements of 6A; there is a decrease of ν_1 upon passing from molybdenum complexes to the corresponding uranium peroxo complexes. The different data show that for the $M(O_2)$ grouping the ν_1 (O-O) modes decrease with the increase in the atomic number of metals in a particular group.

(7) The molar conductance values indicate that the complexes are non-electrolytes in solution.

(8) The ν_1 mode of the peroxo complexes of Zr(IV), Th(IV), Mo(VI), W(VI) and U(VI) ions containing quardridentate ligands appear at lower frequencies than the peroxo complexes of these metals containing mono-dentate, bidentate and tridentate ancillary ligands. This is presumably due to greater charge neutralization of the metal centres by the quardridentate dinegative σ-donor ligands, causing a weaker coulombic interaction in the $M^{n+}\_O^{2-}_2$ moiety (n=4 or 6)

(9) Bidentate uninegative ligands form seven fold co-ordination with Mo(VI), W(VI) and U(VI) ions whereas bidentate dinegative ligands form 6-Coordinated complexes with Mo(VI), W(VI), U(VI) ions. Zr(IV) and Th(IV) ions form six coordinated complexes with bidentate-dinegative, bidentate-neutral and quardridentate dinegative ligands. However, the macrocyclic legands

(quardridentate neutral) form complexes with U(VI), the structure of which can not be ascertained without having single crystal data on these. Repeated attempts to develop single crystal of the complexes failed.

(10) Oxidizing properties of the peroxo complexes depend on the size of the central metal atom. It has been observed that the oxidizing power increases with the increase in the atomic number of metals in a particular group. This is attributed to its tendency to expand the coordination numbers.

(11) The reactivity of the peroxo complexes also depend on the donicity of the ancillary ligands used. It was observed that peroxo complexes containing $OAsPh_3$ is slightly more labile toward PPh_3 and $AsPh_3$ than that having $OPPh_3$ as a coligand.

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