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CHEMISTRY OF PEROXY-METAL COMPOUNDS: ASPECTS OF CURRENT RESEARCH*

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Intrinsic importance of and specific interest in the chemistry of peroxy-metal compounds have been highlighted, and an attempt has been made to draw attention to the biochemical connection of heteroligand peroxy-transition-metal complexes. A comprehensive account of important recent development in the field of synthesis and strucutral assessment of heteroligand peroxy compounds of titanium, zirconium, vanadium, chromium, copper, and uranium has been presented. A few reactions of peroxy-metal compounds, as typical examples of their involvement in the activation of transfer of oxygen, have been summarized.

Key Words : Biochemical Relevance of Peroxy-Metallates: Synthesis of Peroxy-Metal Complexes; Reactivity of Coordinated Peroxide

INTRODUCTION

IT has been known for over a century that characteristic colour reactions may take place when hydrogen peroxide is added to solutions of transition metal derivatives,[1] and some peroxy-transition-metal compounds have been isolated in the solid state. Peroxy-metal compounds, besides having an intrinsic interest of their own,[2–23] are of considerable growing importance particularly in relation to the catalysis of oxidation[24] involving H_2O_2[25] itself, and the storage and transport of oxygen in biological systems.[26,27] To be classified as a peroxymetallate, it is necessary that at least one O_2^{2-} ligand be present in the metal compound.

Although the chemistry of these compounds embraces a fascinating and worthwhile area of investigation, this report is limited to a discussion of those peroxy complexes that are of interest as representatives of heteroligand peroxy compounds of metals. *Per force*, this report deals mainly, but not exclusively, with heteroligand peroxy complexes containing the elements titanium, zirconium, vanadium, chromium, copper, and uranium.

In presenting this report, which takes note of the literature through the middle of 1985, no attempt has been made to make a complete coverage of all aspects of the problem. Rather the effort has been directed to approach the subject in such a way as to complement the work of interest in the context of synthesis and structural assessment. Specifically, the attention has been focused largely on to the synthetic approaches that have been made to obtain peroxy-metal complexes of the

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aforesaid metals. Some results of studies of reactivity coordinated peroxide have also been included here.

Terminology and Nature of O_2

Although the term molecular oxygen refers to the free uncoordinated O_2 molecule with the ground state $^3\Sigma_g^-$, the term dioxygen has been used as a generic designation for the O_2 moiety in any of its several forms, and can refer to O_2 in either a free or a combined state.[28] For use of this term, it is essential that a covalent bond has to exist between the two oxygen atoms. Thus, in general a metal-dioxygen complex refers to a metal containing O_2 group(s) coordinated to the metal centre, and no distinction is made between neutral dioxygen or dioxygen in any of its reduced forms (O_2^- or O_2^{2-}). Accordingly, a peroxy-metal complex is one in which the coordinated dioxygen resembles a peroxide (O_2^{2-}) anion.[26] The incorporation of O_2 into a metal complex to form a metal-dioxygen compound is called *oxygenation*, and the reverse is known as *deoxygenation*.

Molecular oxygen is a paramagnetic molecule having a triplet $^3\Sigma_g^-$ ground state. An MO description of $^3\Sigma_g^-$ level is O_2 $KK(2s\,\sigma_g)^2\,(2s\,\sigma_u^*)^2\;\;(2p\sigma_g)^2\;\;(2p\pi_u)^4\;(2p\pi_g^*)^1\,(2p\pi_g^*)^1$, where KK term signifies that the K shells of two oxygen atoms are filled. The two unpaired electrons in the $^3\Sigma_g^-$ ground state occupy one each of the two degenerate antibonding $2p\pi_g^*$ orbitals, leaving O_2 with a formal bond order of two. The addition of one or two electrons to a neutral O_2 results in formation of the superoxide (O_2^-)and peroxide (O_2^{2-}) respectively, leaving O_2^- with a bond order of 1.5, and the peroxide O–O link with a normal bond order of one. Some of the salient features for O_2, O_2^- and O_2^{2-} are summarized in Table I.

Table I

Some properties of O_2, O_2^- *and* O_2^{2-}

	Bond order	Compound	O—O distance Å	Bond Energy (kcal/mole)	$\nu_{(O-O)}$ (cm^{-1})
O_2	2	O_2	1.207[29]	117.2	1554.7[31]
O_2^-	1.5	KO_2	1.28	—	1145[32]
O_2^{2-}	1	Na_2O_2	1.49[30]	48.8	842[33]

Mode of Coordination of Peroxide (O_2^{2-}) and Structure in the Solid State

The way in which a peroxo group is expected to coordinate to metals[27] can range symmetrical bidentate to a terminal monodentate position, including all from a the possible angles in between (Fig 1).

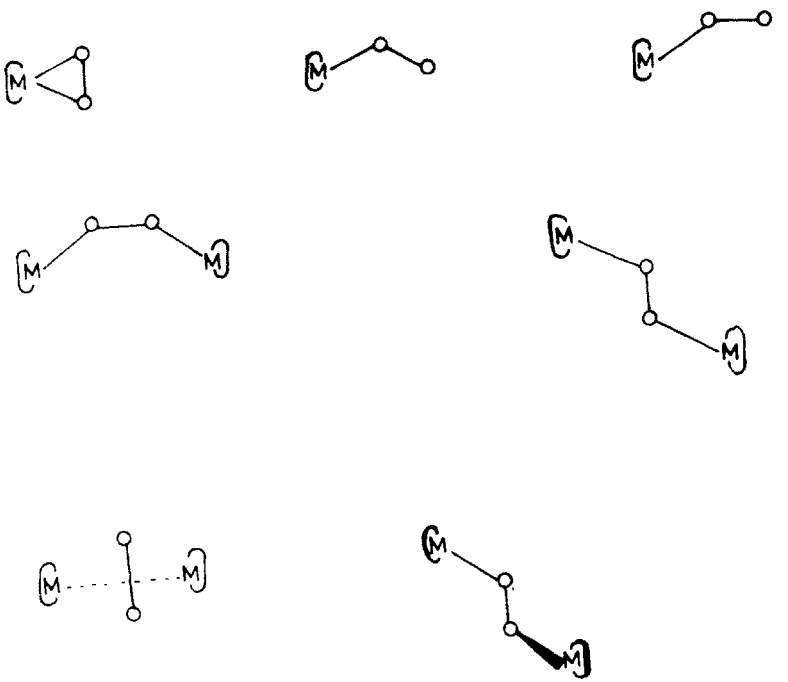

FIG 1

The bridging μ-peroxo could vary from *cis*-planar and *trans*-planar to *trans*-non-planar configurations. An unusual symmetrical double bridging was also found.[34] Deviations from the ideal symmetry are not uncommon. In the case of the hetero-ligand fields the deviations are due to the inherent symmetry of different donor atoms. Additional $p\pi^*$ electron delocalization to the metal ion is anticipated which would therefore favour a d^0 or a low d^n metal ion configuration.

The stereochemical polyhedra in heteroligand peroxy complexes are fairly predictable. For the second row elements Nb and Mo for example, coordination numbers 8 with a dodecahedral (D_{2d}) symmetry has invariably been observed in the absence of oxo groups. In oxoperoxy-heteroligand surroundings the pentagonal bipyramidal arrangement is the most common,[35,36] usually with two coordinated peroxo groups[35] in the *cis* positions and an oxo group in an axial position. There are also three interesting non-octahedral examples[27] of coordination number 6 for chromium, vanadium[37] and titanium complexes. The tetraperoxychromate (V), $[Cr(O_2)_4]^{3-}$ has been shown to have a dodecahedral structure,[38] and it is believed that the vanadium complex $[V(O_2)_4]^{3-}$ should have and an analogous structure.[39] It must be remarked that very little has been done on structural analysis of peroxy-metal complexes, except for some of heteroligand peroxy compounds,[40–42] and studies in this direction are required.

Importance of Vibrational Spectroscopy

Infrared spectroscopic studies are essential and Raman spectroscopic studies are very important for the characterisation and structural assessment of peroxy-metal complexes.[43–50] The peroxy-metal complexes involving a metal-triangular bidentate peroxide (O_2^{2-}) ligand would be expected[51] to give rise to three vibrations of symmetry species ($2A_1 + B_2$), and these may be designated as $\nu_1(A_1$; O–O stretching) $\nu_2(A_1$; symmetric metal—peroxide stretch), and $\nu_3(B_2$; asymmetric metal—peroxide stretch). All the three modes should be active in both the infrared as well as Raman, but the A_1 modes should be polarized and the B_2 mode depolarized in Raman. The $\nu_{(O-O)}$ band is the most sensitive and intense one, and characteristically occurs between 800 and 900cm^{-1}. The frequency of this band remains fairly independent of the heteroligand environment, but is sometimes affected by the mass of the metal centre indicating coupling of the $\nu_{(O-O)}$ with metal–O_2 vibrations. This most familiar way of bonding of O_2^{2-} group, in a triangular bidentate fashion, is similar to that proposed by Griffith[52] for the binding of O_2 in oxyhemoglobin. The dimeric peroxy complex is sometimes more stable than the monomeric complex, and are generally formed unless its formation is inhibited e.g., $(NH_3)_5[CO\text{–}O_2\text{–}CO(NH_3)_5]^{4+}$ The $\nu_{(O-O)}$ for such complexes span a range of 790–844cm^{-1} with an average value of 810cm^{-1} (cf. μ-peroxo).[26]

Heteroligand Peroxy-Metal Complexes

Simple peroxy compounds of metals are the ones which contain peroxides, hydroperoxides, and water molecules, whereas heteroligand peroxy complexes are mixed ligand complexes containing one to three coordinated peroxo groups, and one or more monodentate or polydentate ligands. Heteroligands may range from monodentate halide ions to bulky porphyrin[27] (F^-, Cl^-, NH_3, CO_3^{2-}, SO_4^{2-}, $C_2O_4^{2-}$....., NTA, EDTA..., en, dipy, *o*-phen, oxine..., pyridine-2,6-dicarboxylate... etc.). The stability of peroxy complexes is generally enhanced by specific heteroligand combinations. Thus, many simple transition metal peroxides often explode spontaneously; some are sensitive to shock or decompose above 0 °C, and several do not exist at all as stoichiometric compounds.[1] Many heteroligand peroxy complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating *in vacuo*, and many remain unchanged for prolonged periods.[23,36,37,40,53–56]

A comparison between the peroxo and unreduced dioxygen heteroligand complexes reveals that the chemistry of the two is very different owing to the presence of two extra electrons in the antibonding O-$p\pi^*$ orbitals of the peroxide ion (O_2^{2-}). The electron rich O_2^{2-} ion therefore preferably forms complexes with metal ions of low d^n electron configuration, while the neutral dioxygen molecule favours higher d^n metal centers. However, there are at least two things that these two oxygen species have in common : (*i*) both are stabilised by specific heteroligand environments; and (*ii*) both are of importance in the context of biochemistry.

The biochemical relevance and significance of peroxy-metal complexes have been emphasized in the literature.[7,23,26,27,57–60] The reactivity of peroxides,[62–68]

and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest in biochemistry, but are not generally easy to measure directly. The importance of metal complexes containing neutral dioxygen, in biochemistry is well known,[26] but the biochemical connection of peroxy-metal complexes with biological processes is not very well understood. It is, however, believed[27] that *peroxides take part in the basic biochemical processes in complex cell systems, and their possible interaction with transition metal ions present in the surroundings is an intriguing problem.* The studies of chemistry of peroxy-metal complexes must serve as the major step towards the understanding of and an insight into this area of biochemistry. The metals : Sc, Ti, V, Cr, Y, Zr, Nb, Mo, La, Hf, Ta, W,[27] and U[69] may form stable heteroligand peroxy complexes, and there is increasing evidence that vanadium has a significant biological rôle.[70–73] It may be stressed that the most interesting aspect of peroxy-metal chemistry, from biochemial point of view, turns out to be the experimental approach to measuring the reactivity of the coordinated peroxo group in environments of various heteroligand fields. The reactivity of coordinated peroxo groups means essentially the case of electron-transfer to and from the dioxygen anion O^{2-}. Synthesis of peroxy-metal compounds is an important prerequisite for the types of studies referred to above.

Thus, the synthesis of well-defined hetroligand peroxy-metal complexes, and the study of their properties provide a heuristic approach to an understanding of the role of metals in the catalytic reactions.

Recent Studies on Peroxy-Metal Complexes Involving Titanium, Zirconium, Vanadium, Chromium, Copper and Uranium

A. Peroxy-titanium Compounds

An acidic solution of titanium(IV) forms an intense orange colour with hydrogen peroxide. The colour of titanium(IV)—H_2O_2 system depends heavily on the *p*H of the reaction solution, being orange in acid, yellow in solution of *p*H *ca* 8, and colourless in strong alkaline media. Although a number of solid peroxy-titanates were isolated, there is little agreement over their formulae and structures. The details of the conflicting literature has been covered in a review.[1] The better characterised species, among the relatively older examples, include the heteroligand peroxy-titanates of the types A_3 [$Ti(O_2)$ F_5], A_2 [$Ti(O_2)$ $(SO_4)_2$]. n H_2O (A = Li, Na, K or NH_4)[44,45,74] and A_2 [$Ti(O_2)$ $Cl_4(H_2O)$] (A = Rb or Cs).[74] The peroxyfluorotitanate, $(NH_4)_3$ [$Ti(O_2)F_5$], was obtained by treating a concentrated solution of $(NH_4)_2$ TiF_6 with hydrogen peroxide at 20 °C, and then with cold ammonia. The $(NH_4)_3$ [$Ti(O_2)$ F_5] complex is isomorphous with $(NH_4)_3$ [$Nb(O_2)$ F_5] and $(NH_4)_3$ [ZrF_7], and accordingly the central titanium atom is presumed to be seven-coordinate.

Taking into account of the effect of *p*H, of reaction media, on the course of reaction between titanium (IV) and hydrogen peroxide, it has been shown very recently that yellow A_3 [$Ti(O_2)$ F_5] (A = Na, K or NH_4) complexes can be

synthesised directly, following a general procedure,[75] from the reaction of TiO_2 in 40 per cent HF with 30 per cent hydrogen peroxide at *p*H 6 maintained by the addition of the corresponding alkali hydroxide or aqueous ammonia. A new series of peroxyfluorotitanates of the type A_2 [$Ti(O_2)_2$ F_2] (A = K or NH_4), the synthesis of which has been achieved from the reaction of TiO_2 with 40 per cent HF and 30 per cent H_2O_2 at *p*H 9 maintained by the addition of the corresponding *A*OH and then by precipitation with enthanol, has been described in the same report.[75] The diamagnetic A_3 [$Ti(O_2)$ F_5] and A_2 [$Ti(O_2)_2$ F_2] compounds are soluble and permit molar conductance measurements in water with the conductance values being *ca* 360 and *ca* 230 $\Omega^{-1}cm^{-2}$ mol^{-1}respectively. The infrared and Laser Raman spectra of the complexes suggest that the peroxide (O_2^{2-}) groups are bonded to the titanium(IV) centre in a triangular bidentate(C_{2v}) manner, and the complex species $[Ti(O_2)F_2]^{3-}$ and $[Ti(O_2)_2$ $F_2)]^{2-}$ retain their structural identity also in solutions. A clear shift of $\nu_{(O-O)}$ (ν_1) mode of the coordinated peroxide from *ca* 900 to *ca* 850cm^{-1} in going from $[Ti(O_2)$ $F_5]^{3-}$ to $[Ti(O_2)_2$ $F_2]^{2-}$ is a clean indication of a decrease in O–O bond order with increase in the number of coordinated O_2^{2-} groups. The $\nu_{(Ti-F)}$ has been observed as a medium intensity band at *ca* 430cm^{-1} in the IR spectra, while the band at *ca* 250cm^{-1} both in the IR as well as in the Raman spectra most likely owes its origin to a Ti-F deformation mode. The synthesis and assessment of molecular structure by IR and Laser Raman spectroscopy of potassium trifluroperoxytitanate(IV) trihydrate, K [$Ti(O_2)$ F_3]. H_2O, has been the subject matter of a recent paper.[76] The reaction of TiO_2 in 40 per cent HF with hydrogen peroxide and an excess of KOH followed by adjusting the *p*H of the reaction medium at *ca* 8 by the careful addition of 40 per cent hydrofluoric acid has led to the successful synthesis of K [$Ti(O_2)$ F_3]. 3 H_2O in high yields. The fact that the $\nu_{(O-O)}$ (ν_1) and the complementary $\nu(Ti-O_2)$ (ν_2 and ν_3) modes in the IR and Laser Raman spectra were observed in the positions stipulated for a triangularly bonded peroxide, renders it certain that the peroxide (O_2^{2-}) is bonded to the Ti(IV) centre in a chelated manner. The complex [$Ti(O_2)$ F_3]$^-$ may be a pentacoordinated monomer, however, it is more likely that it has an octahedral or a distorted octahedral structure through—Ti-F-Ti-interactions. It is believed, in view of the methods of syntheses of the complex species [$Ti(O_2)$ F_5]$^{3-}$, $[Ti(O_2)_2$ $F_2]^{2-}$ and [$Ti(O_2)$ F_3]$^-$, that TiO_2 dissolves in aqueous hydrofluoric acid producing flurotitanate(IV) in solution which subsequently undergoes peroxygenation in the presence of H_2O_2 at different *p*H to afford the various peroxyfluorotitanates(IV) as described above.

It is remarkable that titanium forms the best characterised[23] mononuclear metalloporphyrin peroxy complex TiTPP (O_2).[7] The IR spectrum of TiTPP(O_2) shows $\nu_{(O-O)}$ at 895 cm^{-1}, characteristic of peroxide complexes,[2] which shifts to 857cm^{-1} with $^{18}O_2$ substitution. This and the other evidences establish that the dioxygen exists in its reduced form of peroxide (O_2^{2-}). Miksztal and Valentine[23] have studied the reaction of SO_2 and TiTPP(O_2), and showed that SO_2 is oxidised by the coodinated peroxide and TiTPP (SO_4) is formed. The ν_3 modes of sulphate lie at 1325, 1182 and 985cm^{-1}. A comparison with the other sulphate complexes

shows that these vibrations occur at relatively higher energies for ν_3 vibrations, and therefore suggests that sulphate is bound to the titanium centre in a chelating bidentate manner. A structurally characterised, unusually stable peroxytitanium(IV) compound, peroxy *bis* (picolinato) (hexamethylphosphorictriamide-titanium(IV) has been described in 1982.[77] The X-ray crystal structure essentially revealed that the O—O distance in peroxy group is short and hexamethylphosphorictriamide (HMPT) is weakly bonded to titanium. Strong stabilization of the peroxytitanium moiety by picolinato ligand precluded oxygen transfer from the compound to organic substrates.

The synthesis of alkali diperoxymorosulphatotitanate(IV) tetrahydrates, A_2 $[Ti(O_2)_2SO_4].4H_2O$ (A = K or NH_4), has been accomplished[78] by reacting freshly precipitated hydrated titanium dioxide with 7.65(M) sulphuric acid and 30 per cent hydrogen peroxide at *p*H 2.5 adjusted by the addition of KOH or aqueous ammonia. The results of structural assessment of the yellow, microcrystalline, and diamagnetic A_2 $[Ti(O_2)_2SO_4].4H_2O$ involving IR and Laser Raman (LR) spectroscopy show that each of the O_2^{2-} and SO_4^{2-} ligands in the complex $[Ti(O_2)_2SO_4]^{2-}$ ion is bonded to the Ti^{IV} centre in a bidentate chelating manner. The compounds start losing H_2O at *ca* 120 °C, a temperature at which peroxide is also lost.

B. Peroxyzirconium Compounds

Very little is known about peroxy compounds of zirconium. Whenever the subject is under discussion, a frequent reference is made to the sparingly soluble hydrated peroxide, $ZrO(O_2).nH_2O(n \geqslant 2)$ which is obtained[1] by treating Zr^{4+} salts with hydrogen peroxide. It has been mentioned in passing that an anionic species such as $[ZrO(O_2)_2]^{2-}$ probably exists in strong alkali. The heteroligand peroxyzirconates reported so far include peroxysulphatozirconates(IV) of variable compositions,[79] $Zr(O_2)(C_2O_4)(H_2O)_6$,[80] and $(NH_4)_3[Zr(O_2)F_5].H_2O$.[51] The peroxypentafluorozirconate (IV) complex $(NH_4)_3[Zr(O_2)F_5].H_2O$ was synthesized by dissolving freshly prepared hydrated zirconium oxide in 40 per cent hydrofluoric acid, adding an excess of 30 per cent hydrogen peroxide, and then adding aqueous ammonia (at the temperature below 0 °C) until the *p*H reached 7. The $\nu_{(O-O)}$ was reported as a weak band at 839 cm^{-1} in the IR spectrum.[51]

A systematic investigation has just been initiated in the field of peroxyzirconates. Two series of peroxyfluorozirconates(IV) of the types A_2 $[ZrO(O_2)F_2]$ (A = Na, K or NH_4) and A_3 $[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4) have been synthesised.[81] The syntheses have been achieved by reacting a suspension of freshly prepared hydrated zirconium oxide in an excess of hydrogen peroxide with a small amount of 40 per cent hydrofluoric acid followed by adjusting the *p*H at 6 and at 12–14 respectively. While *p*H 6 is suitable for the synthesis of the monoperoxy complex $[ZrO(O_2)F_2]^{2-}$ ion, *p*H 12–14 has been found to be conducive to the synthesis of the diperoxy species $[ZrO(O_2)F]^{3-}$. A notable point emerged out of this study is the lack of formation of any peroxyzirconate, under the reaction condition, upto a *p*H of 5. Indeed the product isolated at *p*H 5 appear to be a salt of the complex species $[F_5Zr\text{-}O\text{-}ZrF_5]^{4-}$. From the limited study it can only be said

that zirconium(IV) undergoes peroxygenation, particularly in the presence of F^-, at *p*H $\geqslant$ 6. The $\nu_{(O-O)}$ for the new peroxyfluorozirconated(IV) has been observed as a medium intensity band at *ca* 850cm^{-1} in their vibrational spectra. A unique feature of the IR spectra of $A_4[F_5Zr\text{-}O\text{-}ZrF_5]$, A_2 $[ZrO(O_2)\ F_2]$ and A_3 $[ZrO(O_2)_2\ F]$ compounds is the appearance of a strong band at *ca* 450cm^{-1} which is attributed to the $\nu_{(Zr-F)}$ mode.

C. Peroxyvandium Compounds

The peroxyvanadium chemistry is generally complicated owing to the formation of different types of complexes with a small variation of acidity/alkalinity of the reaction solutions.[1] The reaction of concentrated alkali with a concentrated solution of V_2O_5 in hydrogen peroxide at low temperatures ($\leqslant$ 0 °C) gives a deep blue solution owing to the formation of tetraperoxyvanadate(V) species,[1] $[V(O_2)_4]^{3-}$. The salts of this complex ion are obtained by the addition of ethanol to such a solution, and are stable only at low temperatures and their stability decreases with increasing cation size.[1] The K_3 $[V(O_2)_4]$ salt is isomorphous with K_3 $[Cr(O_2)_4]$[38] and diamagnetic consistent with the presence of vandium(V). The IR spectra of $(NH_4)_3[V(O_2)_4]$ and K_3 $[V(O_2)_4]$ contain bands in the 800–900cm^{-1} region that have been assigned to $\nu_{(O-O)}$ modes of peroxy groups.[82] It was suggested that slight excess of a base destroys the tetraperoxy species leading to the formation of the anion $[VO(O_2)_3]^{3-}$, $[V(O_2)_4]^{3-} + OH^- \rightarrow [VO(O_2)_3]^{3-} + HO_2^-$ which is stable at room temperature. Triperoxyvanadate(V) complex $[V(O_2)_3]^-$ was not known until 1985.[83] The blue *A* $[V(O_2)_3]$ (*A* = Na or K) compounds have been synthesised from the reaction of V_2O_5 with hydrogen peroxide and alkali hydroxide in a highly alkaline medium ($V_2O_5 : H_2O_2 : AOH$ molar ratio of 1 : 42.5 : (10–12)). The reactions have been conducted at an ice-water temperature and the compounds are obtained by precipitation with ethanol as blue stable products. The *A* $[V(O_2)_3]$ are diamagnetic, and their molar conductances have been found to lie in the range 130–140 Ω^{-1} cm^2 mol^{-1}. The IR and Laser Raman spectra, recorded both on solids as well as in solutions, suggest that the complex $[V(O_2)_3]^-$ species retains its structural identity, and peroxide (O_2^{2-}) ligands are bonded to the metal centre in a triangular bidentate (C_{2v}) manner with the $\nu_{(O-O)}$ (ν_1), $\nu_{(V-O_2)}$ (ν_2) and $\nu_{(V-O_2)}$ (ν_3) modes occurring at *ca* 850, *ca* 530, and *ca* 610 respectively.

The yellow colour produced on addition of hydrogen peroxide to a dilute solution of a metavanadate has been ascribed to the formation of diperoxy anion by cryoscopy[84] as well as by thermo-chemical studies.[85] There was some controversy as to how the complex anion should be formulated, the results of cryoscopic and spectroscopic studies[1] have been interpretated in terms of the anion $[VO(O_2)_2]^-$. Various attempts in past to obtain the complex in the solid state led to failure,[1] and the problem remained. The first suecessful synthesis of oxodiperoxyvanadates (V), *A* $[VO(O_2)_2]$ (*A* = Na, K or NH_4), has been achieved only very recently[86] from the reaction of V_2O_5 with 30 per cent hydrogen peroxide and the corresponding *A*OH, in the concentration ratio 1 : 41.8 : (5.3–6.6), followed by precipitation with ethanol. *p*H 7–8 of the reaction medium has been found to be very

appropriate for the synthesis of the yellow, diamagetic *A* $[VO(O_2)_2]$ complexes. It has been inferred from the results of IR and Laser Raman spectral studies that the complex species $[VO(O_2)_2]^-$ contains a terminally bonded V=O group ($\nu_{(V-O)}$ at *ca* 950scm^{-1}), and that the peroxide (O_2^{2-}) ligands are bonded to the vanadium(V) centre in a chelating fashion with the $\nu_{(OO)}$ (ν_1), $\nu_{(V-O_2)}$ (ν_2) and $\nu_{(V-O_2)}$ (ν_3) being at *ca* 875s, *ca* 525s and *ca* 605scm^{-1} respectively. The $[VO(O_2)_2]^-$, in an aqueous solution undergoes facile addition reactions with F^- and 2,2′-bipyridyl (bipy) to produce $[VO(O_2)_2\ F]^{2-}$ and $[VO(O_2)_2$ bipy$]^-$ complexes respectively.

The addition of hydrogen peroxide to (*i*) V_2O_5,[87] (*ii*) an acid solution of a metavanadate,[88] (*iii*) a vanadium(V) salt in a weakly acid solution,[89] (*iv*) or a decavanadate[90] produces in each case a red colour believed to be due to the formation of a monomeric monoperoxyvanadate (V) cation $[VO(O_2)]^+$. The red colour thus obtained is stable in moderately acidic media. In an excess of hydrogen peroxide the red cation is converted to the yellow oxodiperoxyvanadate(V) anion[89,90] $[VO(O_2)_2]^-$. It was concluded[1] from the results of various studies that

(*i*) the number of peroxy groups per V atom increases with alkalinity;

(*ii*) increasing acidity increases polymerisation and decreases the number of peroxy groups per vanadium atom; and

(*iii*) increasing concentration of H_2O_2 decreases the degree of polymerisation.

There has been a renewed interest in the red colouration that is produced in the reaction of vanadium(V) with hydrogen peroxide in an acidic medium. It was expected that the complex responsible for the above mentioned red colouration might as well be a peroxyvanadate(IV) species, since hydrogen peroxide would probably be able to reduce V^{5+} to V^{4+} in acidic media. It was also thought that the number of peroxy-groups bonded to vanadium in an acidic medium[91] would be less than that in an alkaline medium. In view of the above considerations the reaction between alkali tetrafluorooxovanadates(V),[92] *A* $[VOF_4]$ (*A* = K, Rb, Cs or NH_4) and 6 per cent hydrogen peroxide was carried out and a red solution was obtained. The *p*H of the solution was found to be *ca* 4. The peroxyvanadium complex was isolated in the solid state as its alkali metal salts by addition of ethanol which possibly facilitated the reduction of V^{5+} to V^{4+} and precipitated the complex. This enabled the synthesis of a series of diaquafluorooxodiperoxyvanadates(IV), *A* $[VO(O_2)\ F(H_2O)_2]$ (*A* = K, Rb, Cs or NH_4);[93] these peroxyvanadate(IV) compounds have been obtained for the first time, in the solid state. The orange-red *A* $[VO(O_2)\ F(H_2O)_2]$ complexes slowly decompose in water. The results of peroxide estimation by cerimetry (Ce^{4+}) and also by iodometry conclusively suggest the presence of one O_2^{2-} group coordinated to vanadium(IV) centre. The results of direct titration with a standard $KMnO_4$ solution showed the involvement of three electron equivalents, two of which originated from O_2^{2-} and the third was due to the process $V^{5+} \longrightarrow V^{4+} + e$. The magnetic moment values of the compounds (295 K), lying between 1.70 and 1.75 BM, are consistent with the presence of vanadium(IV). The optical spectra of *A* $[VO(O_2)\ F(H_2O)_2]$ (*A* = K or NH_4) recorded in cold dilute H_2O_2, are in very good agreement with those of oxovanadium(IV) complexes,[94] giving strong evidence

for the presencc of vanadium(IV) in the orange-red peroxyvanadium compounds. These observations also support the recent report[95] concerning the existence of peroxyvanadium(IV) in solutions. The IR spectral band at *ca* 960 scm^{-1} has been assigned to the $\nu_{(V-O)}$ mode of the terminally bonded V=O group, while those at *ca* 890s and *ca* 615scm^{-1} have been assigned to $\nu_{(O-O)}$ and $\nu_{(V-O_2)}$ respectively of the coordinated peroxide. The absorption at *ca* 3160m, br and *ca* 1630 w, br cm^{-1} have been attributed to $\nu_{(O-H)}$ and $\delta_{(H-O-H)}$ modes of coordinated water. The band at *ca* 475cm^{-1} is attributed to a V-F stretching mode; its position indicates the presence of bridging rather than terminal F. It is thus significant to note that the most familiar red colour reaction between vanadium(V) and H_2O_2 in acid media must be attributed to the formation of a monoperoxyvanadate(IV) complex[93,95] and not to a monoperoxyvanadate(V) species as described in the earlier literatures.

Studies on peroxyvanadium chemistry has engaged the attention of many research groups. Whereas most of the recent reports, until 1982, deal with the studies in solutions,[58,59,91,95-98] the synthesis and structural assessment of such compounds have received a rather scant attention. Niobium and tantalum, the congeners of vanadium, form heteroligand peroxy compounds easily and structural analysis of some such niobium complexes show that the coordination polyhedron is dodecahedral.[41] Unlike Nb and Ta, vanadium has a strong tendency to form oxoperoxy species.

Crystalline oxodiperoxyvanadate(V) complexes containing coordinated 2,2′-bipyridyl (bipy), 1,10-phenanthroline(phen), and oxalato groups, $C_2O_4^{2-}$ (*OX*), *A* $[VO(O_2)_2\ L].nH_2O$ (*A* = Na, K or NH_4; *L* = bipy or phen; *n* = 2–5) and A_3 $[VO(O_2)_2\ (OX)].\ 2\ H_2O$ (*A* = K or NH_4), have been reported in 1973.[99] The complexes were synthesised in hydrogen peroxide solutions of trioxovanadate (V) ions in the presence of corresponding heteroligands. The corresponding ethylenediamine (*en*) complexes, $A[VO(O_2)_2en]$ (*A* = Na, K or NH_4), have been synthesised, only very recently,[100] from the reaction of V_2O_5 with hydrogen peroxide and ethylenediamine at *p*H 9, adjusted by the addition of alkali hydroxide or ammonia solution. While *p*H 9 is suitable for the successful synthesis of *A* $[VO(O_2)_2\ en]$ compounds, *p*H 4–5 is conducive to the preparation of the 2,2′-bipyridy and 1,10-phenanthroline complexes.[100] The compounds are soluble in water, where molar conductances have been measured. The results conform to their formulae. The IR and Laser Raman spectroscopic studies [99,100] suggest the presence of terminally bonded V=O group and chelating peroxide ligands. X-ray crystal structures of K_3 $[VO(O_2)_2\ (C_2O_4)].H_2O_2$ and of (NH_4) $[VO(O_2)_2(bipy)].\ 4H_2O$ have been reported[35] in 1983 and it has been concluded that both the complex species have a pentagonal bipyramidal structure. It has been reported[101] that K_2 $[V_2O_3(O_2)_2\ F_2]$ and $K_2[VO(O_2)_2F]$ have been isolated from the reaction of V_2O_5, 40 per cent HF, and H_2O_2 at high acidity and at *p*H 4 respectively. $(NH_4)_2$ $[VO(O_2)\ OHF_2]$[102] has also been prepared from an acidic medium. The reactions of vanadium pentoxide, alkalifluoride, *A*F, and hydrogen peroxide carried out in a slightly alkaline medium (*p*H *ca* 8) and in a highly alkaline medium have led to the syntheses of yellow diperoxy species *A* $[VO(O_2)_2\ F]$ (*A* = Na, K, Rb, Cs or NH_4),[54] and blue triperoxy

complexes $A_2[V(O_2)_3\ F]$ (A = Na, K or NH_4)[55] respectively. The formation of $[V(O_2)_3\ F]^{2-}$ complex is monitored by IR spectroscopy. The total disappearance of the sharp band at *ca* 950cm^{-1} owing to $\nu_{(V-O)}$ indicated the completion of the reaction. The $A_2[V(O_2)_3F]$ was the first case to show that a minimum of three peroxide (O_2^{2-}) groups are required for the formation of blue peroxyvanadate(V).[55] Both A $[VO(O_2)_2\ F]$ as well as A_2 $[V(O_2)_3F]$ are diamagnetic, and the peroxide groups have been shown to be bonded to the vanadium(V) centre in a triangular bidentate manner. They are not stable in water, but can be stored in sealed polyethylene containers. The $\nu_{(V-F)}$ has been observed at *ca* 470cm^{-1}. Two new types of peroxy fluorovanadates(V), $A_2[HV_2O_2(O_2)_3\ F_4].2H_2O$ (A = K or NH_4) and $(NH_4)_3[V_2O_2(O_2))_4\ F].nH_2O$ ($n \approx 2$), have been obtained by crystallising, under various conditions, from the AVO_3—(AF, HF) H_2O_2-H_2O (A = K or NH_4) systems.[56] Vibrational spectra of new complexes have been argued to be consistent with the presence of dimeric anions containing $V(\mu\text{-}O_2)$ V and V-F-V bridges respectively.

The first chloroperoxyvanadate(V) compounds have been reported in 1984.[103] The compounds A_2 $[VO(O_2)_2\ Cl]$ and A_2 $[V(O_2)_3Cl]$ (A = Na, K or NH_4) have been synthesised by reacting V_2O_5 with ACl, alkali hydroxide or aqueous ammonia AOH, and 9 per cent H_2O_2 in the molar ratios of V_2O_5: ACl : AOH : H_2O_2 of 1:2:10:14 and 1:2:15:14 respectively, and the complexes have been precipitated with ethanol. The fact that a very high concentration of the alkaline medium leads to the formation of the triperoxy species $[V(O_2)_3\ Cl]^{2-}$, while the relatively lower concentration of the alkaline medium produces $[VO(O_2)_2\ Cl]^{2-}$, suggests that a very high alkaline medium probably helps replacement of the last oxygen from the $[VO(O_2)_2\ Cl]^{2-}$ by a O_2^{2-} group, thereby favouring the formation of $[V(O_2)_3\ Cl]^{2-}$ or that the oxo oxygen of the $[VO(O_2)_2\ Cl]^{2-}$ species is converted to the third peroxy ligand by abstracting an oxygen of hydrogen peroxide. The vibrational spectra of the peroxychlorovanadates(V) are consistent with their formulae, and are similar to those of the corresponding peroxyfluorovanadates(V).[54,55] The fall in $\nu_{(O-O)}$ frequency in going from the diperoxy- to the triperoxy complexes suggests a decrease in the O-O bond order of the coordinated peroxy ligands with the increase in the number of such groups bound to the vanadium(V) centre. The facile $[VO(O_2)_3\ Cl]^{2-}$ interconversion, which has also been reported,[103] provides a good example of a process that involves basic formation reaction and an acidic dissociation reaction of peroxyvanadium(V) compounds.

Peroxyvanadates(V) of the types $VO(O_2)$ (O-N) LL' (O-N = pyridine-2-carboxylate type bidentate ligands; $L,L' = H_2O$, MeOH or ∂-donor monodentate or bidentate ligands) and $[VO(O_2)\ (Pic)_2]^-$ A^+L (A = H^+, PPh_4^+; L = H_2O, HMPT), where Pic = Picoline and HMPT = hexamethyl phosphortriamide) have been synthesised[104] recently. The crystal structure of $[VO(O_2)\ (Pic)\ (H_2O)]$ has also been presented in the same report. One of the most significant aspects of the work is the reactivity of the compounds. Based on the results of reactivity studies, it has been shown that the compounds qualify as versatile biomimetic reagents for epoxidation of olefins and hydroxylation of alkanes and aromatic hydrocarbons.[104] Some heteroligand peroxyvanadate complexes have been proposed as one of the model

systems for the biochemistry of vanadium[36] by Gordjevic *et al.* Further, they have reported that some of the heteroligand peroxyvanadates (V) have shown antitumor activity. Synthesis, spectra and structure of A [$VO(O_2)$ ($C_4H_5O_4N$)] (A = K or NH_4; $C_4H_5NO_4^{2-}$ = IDA = dianion of iminodiacetic acid, $C_4H_7NO_4$) have been described very recently.[36] X-ray structure analysis of NH_4 [$VO(O_2)$IDA] has been carried out, and it has been shown to represent the first polymeric structure of a transition metal heteroligand peroxy complex.

The crystalline A [$VO(O_2)$ IDA] compounds have been synthesised by reacting iminodiacetic acid, $C_4H_7NO_4$, with V(V) in the presence of hydrogen peroxide. From X-ray crystallography it has been inferred that the vanadium environment, in the complex anion, can be viewed in two ways.[36] The complex polyhedron can be regarded as a distorted pentagonal bipyramid, with V=O at the apical positions and with an equatorially coordinated peroxy group, positioned trans to the coordinated nitrogen, with two carboxylato oxygens closing the pentagonal ring. Another view of the structure is a distorted rectangular bipyramid, formed by coordinated carboxylato oxygens and oxo group in the rectangular plane, with the peroxy group at one apex and nitrogen at the other.

Within the context of the chemistry of peroxyvanadates there are several points which have not been attended to. One point of importance is the mode of binding of sulphate with V(V) in the complex formed in the reaction with hydrogen peroxide in the presence of SO_4^{2-}, a reaction used in the spectrophotometric determination of vanadium. Taking note of this point, reactions of V_2O_5 with alkali sulphate or alkali thiocyanate and hydrogen peroxide have been carried out at *p*H 7–8, maintained by the addition of the corresponding alkali hydroxide or aqueous ammonia. Oxodiperoxyvanadates(V) containing sulphate were obtained as the products. On the basis of various physico-chemical studies, particularly IR and LR spectroscopy, the compounds have been shown to be A [$VO(O_2)_2$] · A_2SO_4(A = K or NH_4),[105] in which SO_4^{2-} does not coordinate with the V(V) centre but it occurs as an ionic species. Whereas the attempts to coordinate SO_4^{2-} with V(V) in the presence of O_2^{2-} ligand were unsuccessful, the simultaneous coordination of carbonate, Co_3^{2-}, and O_2^{2-} with V(V) appeared to be possible. Accordingly, yellow, diamagnetic peroxy-carbonatovanadate(V) complexes, A_3 [$VO(O_2)_2$ CO_3] · $3H_2O$ (A = Na or K), have been synthesised from the reaction of a mixture of V_2O_5 and A_2CO_3 with 30 per cent hydrogen peroxide at *p*H 7–8.[106] IR and Laser Raman spectroscopy are in conformity with the occurrence of coordinated peroxide and coordinated CO_3^{2-} ligands. The complex $[VO(O_2)_2\ CO_3]^{3-}$ ion presumably has a pentagonal bipyramidal structure similar to that of $[VO(O_2)_2\ C_2O_4]^{3-}$ complex.[35]

D. Peroxychromium Compounds

Peroxychromates are better known and probably better characterised than those of any other transition elements. Formation peroxychromates are dependent on the *p*H of reaction media. Four different types of derivatives were synthesised,[1] by carrying out reactions under different *p*H conditions, with their formulae being A_3 [$Cr(O_2)_4$] . AH [$CrO_2(O_2)_2$], $L$$CrO(O_2)_2$ (L = anitrogen base), and $L_3Cr(O_2)_2$

(L = anitrogen base) or $[Cr(O_2)_2(CN)_3]^{3-}$. Peroxychromates have not only varied compositions, but also different colours. These have been thoroughly reviewed by Connor and Ebsworth,[1] and the details are now available even in text books. Several new diperoxychromates(IV) have been described between 1966 and 1968 which include the following compounds : $[Cr(O_2)_2(en)(H_2O)] \cdot H_2O$,[107] $[Cr(O_2)_2$ dien]. H_2O,[107] $[Cr(O_2)_2(NH_3)(en)] \cdot H_2O$,[108] $[Cr(O_2)_2(pn)(H_2O)] \cdot 2H_2O$[108] and $[Cr(O_2)_2(ibn)(H_2O)].H_2O$[108] (en = ethylenediamine, dien = diethylene triamine, Pn = propylenediamine, ibn = isobutylenediamine). One of the important properties of diperoxychromium(IV) compounds in general and of $[Cr(O_2)_2(NH_3)_3]$ in particular is that they are useful starting materials for chromium(III) complexes.[109] The formation of peroxy compounds by chromium in its oxidation states IV, V and VI makes the chemistry of such compounds interesting but relatively more complex than many other transition elements.

Information on the chemistry of heteroligand peroxychromates are rather sparse, as opposed to those of binary peroxy or oxoperoxy complexes of the metal, and studies on this aspect should be considered rewarding. Although cyanodiperoxychromate(IV), e.g. $K_3[Cr(O_2)_2(CN)_3]$, has been known for quite some time, no haloperoxoxychromate seem to have any reported existence. Efforts in this direction has now led to the successful synthesis of two fluoroperoxychromates(IV) of the types $(NH_4)_3[CrO(O_2)_2F] \cdot H_2O$ and $K_3[Cr(O_2)_3F]$.[110] The later complex is possibly the first triperoxy compound of chromium. The compounds have been obtained from the respective fluorochromate(VI), $ACrO_3F$ (A = K or NH_4),[11] by conducting reactions with hydrogen peroxide in the presence of ethanol at pH 10–11. They are brown and crystalline in nature. While the $(NH_4)_2[CrO(O_2)_2F] \cdot H_2O$ decomposes within a few hours, the $K_3[Cr(O_2)_3F]$ can be stored undecomposed for months. Both explode on heating. The results of chemical analyses, IR and LR spectral studies, and magnetic susceptibility measurements are consistent with their formulae. Whereas $(NH_4)_3[CrO(O_2)_2F] \cdot H_2O$ decomposes in water giving NH_4CrO_3F,[111] $K_3[Cr(O_2)_3F]$ decomposes in water-producing potassium dichromate, $K_2Cr_2O_7$, as the major products.

E. Peroxycopper Compounds

Peroxy copper chemistry is still an enigma to chemists. Although there have been several reports on the reaction of copper (II) and hydrogen peroxide, unfortunately there is little agreement as to the formulae and properties of the products. The conflicting literatures have been reviewed in 1964.[1]

Peroxy copper chemistry is intrinsically interesting, because copper is also the metal present in hemocyanine naturally occurring oxygen carrier nonheme proteins.[26] While the copper in deoxyhemocyanin occurs as copper (I), oxyhemocyanin contains copper as copper (II), with every two Cu (II) being bridged by an O_2^{2-} species.[112] Two copper complexes[113,114], capable of reversibly binding dioxygen have been developed as model systems of hemocyanin. On oxygenation, one mole of O_2 is bound for two moles of Cu which suggest the formation of peroxy bridged species (e.g. Cu (II) $-O_2-$ Cu (II)).

In view of this it was expected that it should be possible to synthesise well-defined peroxy copper compounds under suitable conditions. Our endeavour in this direction has now resulted in the synthesis of two rather simple peroxy copper (II) complexes of the types $[Cu_2(O_2)(OH)(H_2O)_2]F$ and $[Cu_2(O_2)(OH)(H_2O)_2]_2SO_4$. Physico-chemical studies have revealed that the peroxide is bridged between the two Cu(II) centres in each case, and μeff/BM has been found to be typically about 1.45 indicating that an antiferromagnetic interaction is operative in the complexes. IR spectrum of $[Cu_2(O_2)(OH)(H_2O)_2]_2SO_4$ is consistent with the occurrence of an ionic sulphate. Reactions of coordinated peroxide involving $[Cu_2(O_2)(OH)(H_2O)]F$ are being studied. Results obtained so far suggest that the complex is capable of oxidising SO_2 and also organic substrates.

F. Peroxyuranium Compounds

Peroxyuranate chemistry is highly complicated[1] owing to the formation of a host of different species with a slight variation of *p*H of the reaction medium. Peroxyuranates containing O_2^{2-} : U ratios of 1 : 1, 1 : 2, 2 : 1, 3 : 1, 3 : 2, and 5 : 2 have been described in the literature,[1] of which $UO_2(O_2)_2, nH_2O$ (n = 2 or 4) is the best characterised example. Reports on heteroligand peroxyuranates are few, except for some on carbonato and oxalato-peroxyuranates.[1] A systematic investigation on the synthesis and structural assessment of heteroligand peroxyuranates has been initiated. Synthesis of $A_2[UO_2(O_2)F_2]$ (A = CS or NH_4),[69] $A_2[UO_2(O_2)F_2]H_2O$ (A = K or Rb),[69] and $A_2[UO_2(O_2)CO_3]H_2O$ (A = Na or K)[106] have been achieved very recently. While the fluoroperoxyuranates (VI)[69] have been synthesised from the reaction of UO_2^{2+} in solution with AF and 30 per cent hydrogen peroxide at *p*H 6.5–7, the carbonatoperoxyuranates (VI)[106] have been obtained by reacting UO_2^{2+} in solution with $AHCO_3$ and an excess of 30 per cent hydrogen peroxide at *p*H 7–8. Vibrational spectroscopy has been used for structural assessment, and it has been shown that the peroxide ligand is coordinated to the uranyl (UO_2^{2+}) centre, in each case, in a triangular bidentate manner, and also eq the complexes contain trans-linked O=U=O groups. The $\nu_{(O-O)}$ falls in the region 850–890cm^{-1}.

Conclusion

In conclusion, it may be stated that although peroxy-metal chemistry has a long history, the realisation of its versatile importance has grown steadily in last ten years or so. Studies involving syntheses, structural assessment, and reactivities of heteroligand peroxy-metal compounds appear to be specifically interesting. Synthesis of well-defined peroxy-metal compounds is an important prerequisite. Albeit some notable progress in the field has been made recently, it continues to be of great value in contemporary inorganic chemistry. There is every indication that interest in this field will continue to increase as more and more peroxy-metal compounds become available for specific purposes.

Ineviatably, this report describes only a part of our research interests in the field of peroxy-element chemistry. Other interests in the field include studies involving nonmetals viz., boron,[115] phosphorous, sulphur etc., and the results of which would probably be of no less importance than those of the metals.

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