Peroxo and Superoxo Complexes of Chromium, Molybdenum, and Tungsten

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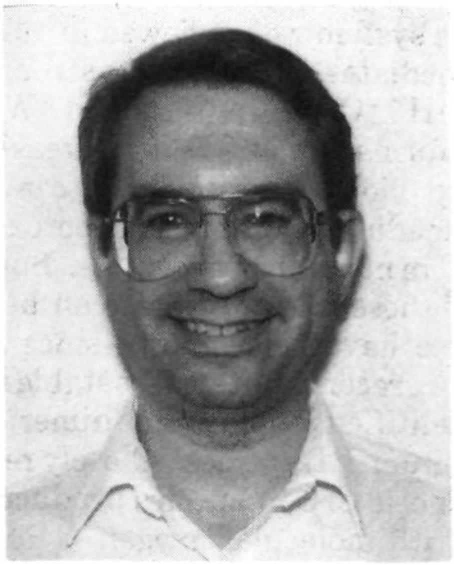
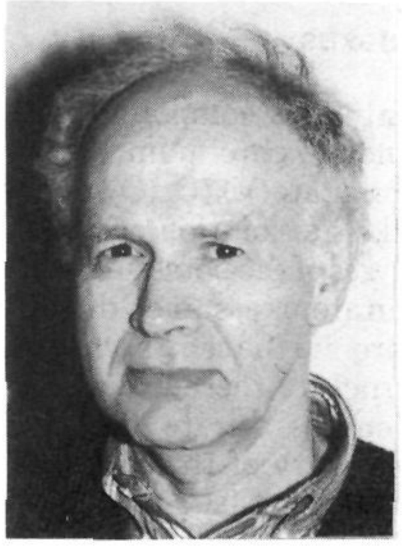
Contents

I. Introduction

Dioxygen complexes of group 6 transition elements have been known since the mid-19th century, when the extraction of the blue peroxochromate into ether was described by Barreswil.[1] The chemistry of peroxy compounds of the transition elements was thoroughly reviewed by Connor and Ebsworth in 1964,[2] and although several articles on specific aspects of dioxygen–transition metal interactions and complexes have appeared, there has been no subsequent review that has focused on complexes of chromium, molybdenum, and tungsten. The present review covers all *characterized complexes* of these three elements that incorporate O–O bonds; dioxygen species that might exist as reaction intermediates are not comprehensively considered. The review is intended to supplement and update that of Connor and Ebsworth, which should be consulted for most earlier references. Certain aspects of this chemistry has since been discussed in articles by Stomberg,[3] Brown *et al.*,[4] Spivack and Dori,[5] Vaska,[6] Gubelmann and Williams,[7] Mimoun,[8] Jørgensen,[9,10] and in Gmelin.[11]



Michael Dickman received his B.S. in Chemistry from the University of Cincinnati in 1977, his Ph.D. in Chemistry from the University of California at Irvine in 1984, and his J.D. from Franklin Pierce Law Center in 1987. He is currently working on polyoxo anion chemistry at Georgetown University.



Michael Pope was born in Exeter, England, and obtained B.A. and D.Phil. degrees from Oxford University with R. J. P. Williams. Following a postdoctoral at Boston University with L. C. W. Baker, and three years with Laporte Industries Ltd. in England, he came to Georgetown University in 1962. He is currently serving as Department Chair.

In general, dioxygen complexes have been classified in terms of their mode of bonding.[6,7] With nonbridging O_2 ligands, both η^1 ("superoxo", O–O ~1.3 Å) and η^2 ("peroxo", O–O ~1.48 Å) examples are known. Bridging dioxygen groups can adopt η^1:η^1 (M–O–O–M), η^2:η^2, or η^1:η^2 configurations. With the few exceptions noted below, the vast majority of dioxygen complexes of Cr, Mo, and W contain nonbridging η^2-peroxo ligands.

In this review the discussion of metal–dioxygen compounds is organized according to the ratio of the number of dioxygen groups to the number of metal atoms.

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II. Chromium

Thirty years ago Connor and Ebsworth could say that the peroxides of chromium were probably better known and better characterized than those of any other transition element. This is much less true today in view of subsequent investigation of other transition metal peroxides.

Many syntheses of dioxygen–chromium compounds start with addition of hydrogen peroxide to a solution of a Cr^{VI} compound. The interaction of aqueous Cr^{VI} species with H_2O_2 is complicated, and work on understanding this system was reviewed in 1970.[4] Reaction rates, intermediates, and products strongly depend on pH. Above pH 7 $[Cr(O_2)_4]^{3-}$ is formed. With increasing acidity, the formation of Cr^{3+} is increasingly favored, but blue and violet intermediates can be observed. These intermediates contain two peroxo groups and are stabilized in nonaqueous solvents. Solid derivatives (adducts) of these intermediates can be isolated and some of these have been known since the late 19th century. More recently, other less stable intermediates have been identified in solution as dimeric and trimeric peroxochromium(III) species. Closely related to these is the monomeric CrO_2^{2+} species produced when Cr^{2+}(aq) reacts with molecular oxygen.

Most of the solid peroxochromates explode when heated or struck, and some have been reported to explode spontaneously at room temperature. Appropriate caution should be used when working with them.

A. 4:1 Complexes

There is only one compound with a 4:1 ratio of dioxygen ligands to chromium. The red-brown anion tetraperoxochromate(V) $[Cr(O_2)_4]^{3-}$ is made by adding H_2O_2 to an alkaline solution of CrO_4^{2-}. X-ray crystal structure analyses of the potassium salt[12,13] K_3CrO_8 show that the oxygen atoms assume a distorted dodecahedral arrangement around the central chromium atom (Figure 1). In this structure there are only two independent Cr–O bond lengths due to the crystallographically imposed $\bar{4}$ symmetry of the anion. The "equatorial" Cr–O bonds are about 0.08 Å longer than the "axial" (Cr–O1 = 1.958 Å, Cr–O2 = 1.882 Å). The O–O bond length of 1.466 Å[13] is slightly shorter than that of the free peroxide ion (1.49 Å[6]).

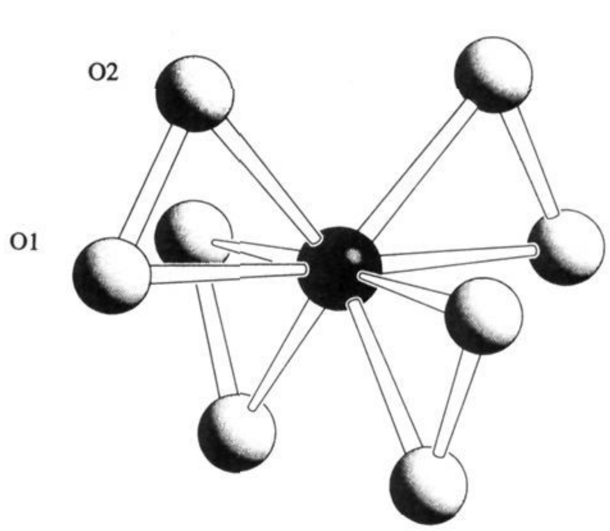

Figure 1. $[Cr(O_2)_4]^{3-}$.

The potassium salt has been investigated as a source of singlet oxygen,[14] and its thermal decomposition has been studied.[15-18] It has also been proposed as an ESR standard.[19,20]

The relatively high symmetry (D_{2d}) of the tetraperoxometalates makes them attractive compounds for theoretical calculations, and there have been several theoretical studies that examine chromium tetraperoxide. Methods used include ab initio,[13,21] EHMO,[22] MS-Xα[23,24] and INDO/1.[25] The calculations are generally in agreement with ligand-field theory,[26] group theory, and experiment[19] in finding that the single unpaired electron occupies an orbital of b_1 symmetry; this orbital is located mainly on the metal, corresponding to an essentially nonbonding chromium $d_{x^2-y^2}$ orbital which has lobes directed between the four in-plane oxygens.

The difference in the Cr–O "axial" and "equatorial" bond lengths has been ascribed to differences in metal d–oxygen π orbital overlap[23] and to a difference in strength of interaction between the 2s atomic orbitals of the two different oxygen atoms with the metal p_z atomic orbital.[25] Since these effects are not mutually exclusive, both may be important.

The decomposition of CrO_8^{3-} in alkaline aqueous solution has been studied. The mechanism appears to proceed through an oxotriperoxo intermediate species, and reversible exchange of peroxide groups between CrO_8^{3-} and H_2O_2 has been demonstrated.[14,27] The overall equation is

$$2H_2O + 4CrO_8^{3-} \rightarrow 4CrO_4^{2-} + 4OH^- + 7O_2$$

At neutral and lower pH the decomposition involves violet and blue oxodiperoxochromate(VI) intermediates.[14,28] The overall equation at pH < 4 is

$$2CrO_8^{3-} + 12H^+ \rightarrow 2Cr^{3+} + 6H_2O + 5O_2$$

and at intermediate pH the final products are mixtures of Cr^{3+} and CrO_4^{2-}. It is possible that the green peroxochromium(III) oligomers that have been reported[29] as intermediates in the reaction of acidic Cr^{VI} with H_2O_2 (see section II.E) might also be formed during CrO_8^{3-} decomposition.

Studies of the interaction of Cr^{VI} with H_2O_2 in acid solution which also produces the blue and violet species (see section II.C) are also relevant to the acid decomposition of CrO_8^{3-}.

B. 3:1 Complexes

There have been no 3:1 complexes characterized for chromium. However, triperoxochromium intermediates have been proposed in the reaction of chromate with H_2O_2 in alkaline solution.[4,27]

C. 2:1 Complexes

1. Oxodiperoxochromium(VI) Species

The 2:1 peroxochromium complexes fall into two main groups: the oxodiperoxo Cr^{VI} complexes and the diperoxo Cr^{IV} complexes. The oxodiperoxo Cr^{VI} complexes are made by treating a solution of CrO_4^{2-} with H_2O_2 at pH 7 or lower. Below pH 4 one of the first products is a blue compound, "perchromic acid" or "peroxochromic acid" which quickly decomposes on standing in aqueous solution, but which can be extracted into nonaqueous solvents (such as ethers, esters, alcohols, ketones, and nitriles) in which it is much more stable. The blue compound has not been isolated in solid form but it is generally acknowledged to be $[Cr(O)(O_2)_2(H_2O)]$, often written as $CrO_5(H_2O)$ or simply CrO_5. After extraction into coordinating nonaqueous solvents the water molecule is apparently replaced by the solvent.[2]

As mentioned above, investigations of the kinetics of the Cr^{VI}–H_2O_2 system were reviewed in 1970.[4] Since then, the kinetics and thermodynamics of the reaction of H_2O_2 with Cr^{VI} in acidic aqueous solution was reexamined using stopped-flow techniques by Tanaka *et al.*[30] In this work the concentration of CrO_4^{2-} was kept low to minimize dichromate formation, and a large excess of H_2O_2 was used. The stoichiometry for the formation of CrO_5 was found to be consistent with the equation

$$HCrO_4^- + H^+ + 2H_2O_2 \rightarrow CrO_5 + 3H_2O$$

with

$$K_f = [CrO_5]/[HCrO_4^-][H^+][H_2O_2]^2 = (2.0 \pm 0.2) \times 10^7\ M^{-3}$$

at 25 °C. The rate law is third order overall

$$-d[HCrO_4^-]/dt = k[HCrO_4^-][H^+][H_2O_2]$$

with $k = 10^{7.6\pm0.2} \exp[(-19 \pm 1\ 1\ \mathrm{kJ}/RT]\ M^{-2}\ s^{-1}$. This implies a mechanism with a monoperoxo intermediate:

$$HCrO_4^- + H^+ \rightleftarrows H_2CrO_4 \quad \text{(fast equilibrium, } K_B\text{)}$$

$$H_2CrO_4 + H_2O_2 \rightarrow \text{“}H_2CrO_5\text{”} + H_2O \quad \text{(rate-determining, } k_2\text{)}$$

$$\text{“}H_2CrO_5\text{”} + H_2O_2 \rightarrow CrO_5(H_2O) + H_2O \quad \text{(fast, } k_3\text{)}$$

The nature of “H_2CrO_5” is undefined, possibilities include $[CrO(O_2)(OH)_2]$, $[CrO_2(OOH)(OH)]$, and $[Cr(O)_2(O_2)(H_2O)]$.

The rate law for the decomposition of CrO_5

$$2CrO_5 + 6\ H^+ \rightarrow 2Cr^{3+} + 3O_2 + H_2O_2 + 2H_2O$$

was reported as

$$-d[CrO_5]/dt = k_1[CrO_5][H^+] + k_2[CrO_5H^+][H^+]$$

with $k_1 = 0.25 \pm 0.02\ M^{-1}\ s^{-1}$ and $k_2 = 1.8 \pm 0.3\ M^{-1}\ s^{-1}$ at 25 °C. The second term of this rate law is consistent with earlier work of Orhanović and Wilkins,[31] who found

$$-d[CrO_5]/dt = k[CrO_5][H^+]^2$$

while the additional first term, $k_1[CrO_5][H^+]$, is apparently a consequence of the more extensive set of data used by Tanaka *et al.* which includes more data points in the less acidic region.

In weakly acidic solution (pH 2.5–5.5) in an isothermal stirred tank reactor, complicated kinetic behavior has been observed for the interaction of Cr^{VI} with H_2O_2, including bistability, hysteresis, and oscillation.[32]

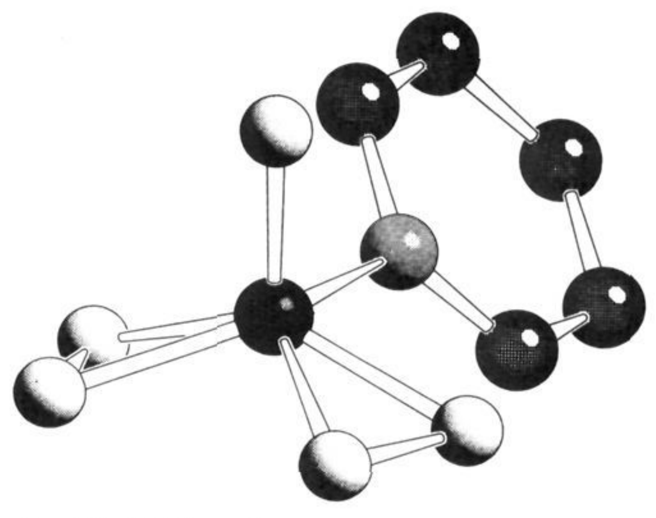

Figure 2. $[CrO(O_2)_2py]$.

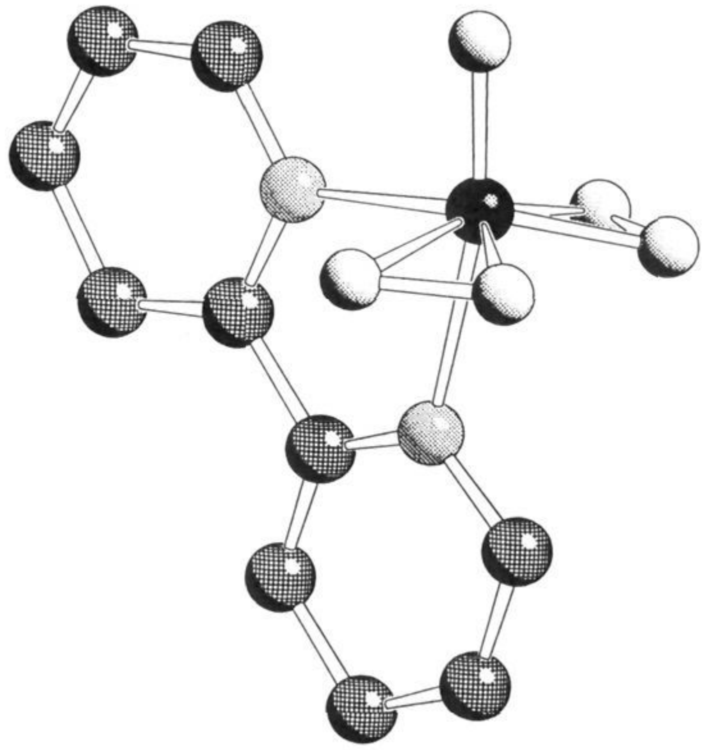

Figure 3. $[CrO(O_2)_2bipy]$.

Table 1. Structurally Characterized Diperoxo Complexes of Chromium(VI), $CrO(O_2)_2L_{eq}L_{ax}$

L_{eq}	L_{ax}	ref
py		*a*
$^1/_2$phen	$^1/_2$phen	*b*
$^1/_2$bipy	$^1/_2$bipy	*c*

[a] Stomberg, R. *Ark. Kemi* **1964**, *22*, 29–47. (b) Stomberg, R. *Ark. Kemi* **1965**, *24*, 111–31. (c) Stomberg, R.; Ainalem, B. *Acta Chem. Scand.* **1968**, *22*, 1439–51.

Addition of bases such as pyridine,[33] aniline,[33] 2,2′-bipyridine,[34] quinoline,[35] pyridine oxide,[36] triphenylphosphine oxide,[36] hmpt,[37] and 1,10-phenanthroline[38] to CrO_5 in ether solution yields adducts which can be obtained in solid form by evaporation of solvent. The adducts are generally more stable than the parent compound. An X-ray crystal structure analysis of the pyridine adduct[39] shows the coordination geometry of the Cr atom to be a distorted pentagonal pyramid with the pyridine nitrogen and two bidentate peroxo groups in the basal plane and an apical oxo group (Figure 2). In adducts of bidentate bases such as 2,2′-bipyridine (Figure 3) and 1,10-phenanthroline, the second nitrogen is coordinated trans to the oxo group and has a significantly longer (by *ca.* 0.15 Å) Cr–N bond compared with that of the equatorial nitrogen. The structurally characterized derivatives of CrO_5 are listed in Table 1. The O–O distances in the oxodiperoxo Cr^{VI} complexes are all about 1.40 Å, while they range from 1.42 to 1.46 Å with a mean of 1.45 Å in the diperoxo Cr^{IV} complexes.[3]

No compound in Table 1 exhibits Cr–O peroxo bonds that differ significantly in length, in contrast to the reported values for CrO_8^{3-}. An oxygen-17 NMR investigation of $CrO_5(py)$ and $CrO_5(hmpt)$ showed two distinct ^{17}O signals for the (structurally inequivalent) peroxo oxygens.[40]

Blue CrO_5 derivatives have been used as oxidants in organic synthesis but generally as stoichiometric rather than catalytic reagents. Ethereal CrO_5 produces a keto lactone from tetracyclone,[41] while $CrO_5(py)$ selectively oxidizes alcohols to carbonyl compounds.[42,43]

Oxidation of tertiary amines Et_3N and p-$MeOC_6H_4NMe_2$ by $CrO_5(hmpt)$ and $CrO_5(Ph_3PO)$ to give N-oxides was studied. The second-order rate law as well as NMR evidence suggested a mechanism involving preliminary coordination of substrate to chromium.[44] In contrast, no NMR evidence for preliminary coordination was found in the nearly quantitative oxidation of organic sulfides to sulfoxides by the same oxidants, although this reaction also followed a second-order rate law (first-order in both oxidant and substrate).[37]

In the oxidation of various hydrocarbons to alcohols by $CrO_5(Et_2O)$ and $CrO_5(Ph_3PO)$ little or no epoxidation or arene hydroxylation was observed. There was, however, some evidence for a catalytic cycle in the oxidation of cyclohexene to cyclohexanol and cyclohexenone.[36]

Initial epoxidation was suggested as the mechanism of oxidation of enol ethers by $CrO_5(py)$, with 1,2-dioxetanes being the major isolated final product in about 20% yield.[45]

Three peroxochromium compounds CrO_5L (L = Et_2O, bipy, py) were evaluated as stoichiometric oxidizing agents for a variety of organic substrates. Alcohols were converted to the corresponding carbonyl compounds, but with 1,2-diols C–C bond cleavage occurred. Decarboxylation of α-hydroxy acids proceeded quantitatively. Oximes were converted to carbonyl compounds, thiols to disulfides, dihydroxy phenols to quinones, benzylamine to benzaldehyde, aromatic amines to azo compounds, and anthracene and phenanthrene to quinones.[43]

Various salts of $[CrO_5(X)]^-$ (X = Cl, Br) have been reported with cations such as triphenylmethylarsonium,[46] tetraphenylarsonium, tetraphenylphosphonium, 2,3,5-triphenyltetrazolium and cetylpyridinium,[47] and potassium-crown ether[48] but no X-ray crystal structure analyses have been reported. Presumably the halogen is coordinated in the basal plane of a pentagonal pyramid as with the pyridine adduct.

When H_2O_2 is added to a solution of Cr^{VI} between pH 4 and 7, an unstable violet solution is formed.[49] Violet salts can be made by treating CrO_5 in ether with small amounts of bases such as NH_3, KOH, and KCN.[2] Since the work of Griffith on the anhydrous potassium salt[50] it has been generally accepted that these are salts of the anion $[CrO_5(OH)]^-$, formally derived from $CrO_5(H_2O)$ by loss of a proton. The violet $[CrO_5(OH)]^-$ anion can also be made by adding CrO_8^{3-} to a neutral solution of H_2O_2. This reaction probably accounts[28] for the discrepancy[2] in visible spectra found for CrO_8^{3-} in neutral solution as opposed to basic H_2O_2 solution.

It seems likely that the OH^- group would be coordinated in the base of a distorted pentagonal pyramid in a fashion analogous to the pyridine derivative of CrO_5. However, no X-ray structural analysis of a violet salt has yet been reported, and with the exception of kinetics studies little work has been done on these compounds in the past 30 years. The violet salts in general tend to be even less stable than the blue CrO_5 derivatives.

The synthesis of a violet solid formulated as triphenylmethylarsonium peroxychromate, $(TPMA)CrO_5(OH)$, has been reported.[46] It was made by adding K_2CrO_4 to a mixture of triphenylmethylarsonium chloride and H_2O_2 in acid solution at −4 °C. A conductometric titration indicated the presence of one proton, and addition of a proton changed the color from violet to blue as would be expected for a $[CrO_5(OH)]^-$ derivative. However, no O–H peak at 3500 cm^{-1} was found in the IR. The explanation suggested[46] was that the proton in these compounds bridges two oxygen atoms, forming an intramolecular hydrogen bond. It was further suggested that the O–H peak at 3500 cm^{-1} observed for the anhydrous potassium salt[50] possibly resulted from contamination by KOH. Thus it appears that the question of the placement of the proton in $[CrO_5(OH)]^-$ derivatives has not been entirely resolved.

The kinetics of $[CrO_5(OH)]^-$ formation has been studied in aqueous solution using a stopped-flow method.[49] The third-order rate law reported was analogous to that found previously for the formation of blue peroxochromate $CrO_5(H_2O)$,[30,31,51] and the proposed mechanism is identical except for the final deprotonation

$$\text{“}H_2CrO_5\text{”} + H_2O_2 \rightarrow [CrO_5(OH)]^- + H_2O + H^+ \qquad (\text{fast}, k_3')$$

The observed k would still be k_2K_B as was reported for the formation of $CrO_5(H_2O)$.

2. Diperoxochromium(IV) Species

These are of general formula $Cr(O_2)_2L_3$, and are usually greenish in color. Compounds of this type are known for L = NH_3 or CN^- as well as tridentate nitrogen bases and mixed ligands such as ethylenediamine and water. They are generally prepared by treatment of CrO_5 species with an excess of the appropriate base, by addition of H_2O_2 and base to CrO_3, or addition of base to $[Cr(O_2)_4]^{3-}$.[2]

Like the oxodiperoxochromium(VI) compounds these are pentagonal bipyramidal complexes with the peroxo oxygens occupying four of the five planar pentagonal coordination sites. Figure 4 shows the structure of $[Cr(O_2)_2(NH_3)_3]$,[52] and Table 2 lists the reported examples of these complexes.

While the ammine and cyano derivatives are relatively stable, some of the other compounds are capable of exploding spontaneously at room temperature. It should also be noted that the existence of a hexamethylenetetramine derivative[53] is considered doubtful in view of a later unsuccessful attempt to synthesize it.[54] A variety of other amines have been used in attempts to form diperoxochromium(IV) complexes but without success.[54]

The 4+ oxidation state is unusual for chromium and there has been much interest in diperoxochromium(IV) complexes. These undergo redox decomposition easily in acidic aqueous solution with evolution of dioxygen to form six-coordinate Cr^{III} complexes.[55] In

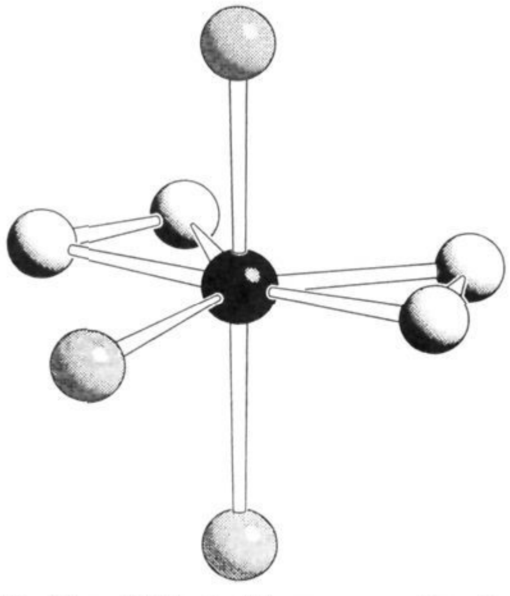

Figure 4. $[Cr(O_2)_2(NH_3)_3]$ (H atoms omitted).

Table 2. Diperoxochromium(IV) Complexes, $Cr(O_2)_2L_3$

L_{ax1}	L_{eq}	L_{ax2}	ref(s)
NH_3	NH_3	NH_3	*a,b*
CN^-	CN^-	CN^-	*c,d*
H_2O	$^1/_2$en	$^1/_2$en	*e,f*
NH_3	$^1/_2$en	$^1/_2$en	*g,h*
H_2O	$^1/_2$pn	$^1/_2$pn	*g,h*
H_2O	$^1/_2$ibn	$^1/_2$ibn	*g,h*
$^1/_3$dien	$^1/_3$dien	$^1/_3$dien	*i,j*

[a] Wiede, O. F. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2178. [b] Stomberg, R. *Ark. Kemi* **1964**, *22*, 49–64. [c] Wiede, O. F. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 378. [d] Stomberg, R. *Ark. Kemi* **1965**, *23*, 401–30. [e] Holmann, K. A. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 3181. [f] Stomberg, R. *Ark. Kemi* **1965**, *24*, 47–71. [g] House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1967**, *6*, 1077–82. [h] Ebsworth, E. A. V.; Garner, C. S.; House, D. A.; Hughes, R. G. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 61–5. [i] House, D. A.; Garner, C. S. *Nature* **1965**, *208*, 776. [j] House, D. A.; Garner, C. S. *Inorg. Chem.* **1966**, *5*, 840.

1 M $HClO_4$ the complexes $[Cr(NH_3)_3(O_2)_2]$, $[Cr(en)(NH_3)(O_2)_2]$, $[Cr(pn)(H_2O)(O_2)_2]$, and $[Cr(ibn)(H_2O)(O_2)_2]$, yield $[Cr(NH_3)_3(H_2O)_3]^{3+}$, $[Cr(en)(NH_3)(H_2O)_3]^{3+}$, $[Cr(pn)(H_2O)_4]^{3+}$, and $[Cr(ibn)(H_2O)_4]^{3+}$, respectively.[54,56] With HCl, replacement of peroxo ligands by both H_2O and Cl^- occurred.[54]

The compounds $[Cr(en)(NH_3)(O_2)_2]$ and $[Cr(dien)(O_2)_2]$ have been the subjects of several kinetics studies.[57] The reaction of $[Cr(O_2)_2(en)(H_2O)]$ with I^- to produce I_2 and $[Cr(H_2O)_4(en)]^{3+}$ probably occurs through the initial dissociative process

$$[Cr(O_2)_2(en)(H_2O)] \rightarrow [Cr(O_2)_2(en)] + H_2O$$

$$[Cr(O_2)_2(en)] + I^- \rightarrow [Cr(O_2)_2(en)I]^-$$

however, an I_d ion-pairing mechanism could not be ruled out.

The kinetics of the acid decomposition of $[Cr(O_2)_2(en)(H_2O)]$ and $[Cr(O_2)_2(dien)]$ were examined.[58] For the former, the products were $Cr_2O_7^{2-}$, $[Cr(H_2O)_6]^{3+}$, and $[Cr(en)(H_2O)_4]^{3+}$. For $[Cr(O_2)_2(dien)]$ only small amounts of Cr^{VI} and $[Cr(H_2O)_6]^{3+}$ were found, the main product being the pink complex $[Cr(dienH)(H_2O)_4]^{4+}$, characterized by electronic spectra and isolated by ion chromatography. Both acid decomposition reactions also produced H_2O_2, O_2, and O_2H, this last radical species having been trapped with tetranitromethane.

Two stages have been observed in the reactions of H_2O_2 with $[Cr(O_2)_2(en)(H_2O)]$ and $[Cr(O_2)_2(dien)]$ in acid solution.[59] The first was production of a blue CrO_5L intermediate and the second stage was the decomposition of this intermediate. Since $[Cr(O_2)_2(en)(H_2O)]$ reacted faster with H_2O_2 than did $[Cr(O_2)_2(dien)]$, a dissociative mechanism analogous to the reaction of $[Cr(O_2)_2(en)(H_2O)]$ with I^- (see above) was hypothesized. The final product of the reaction of $[Cr(O_2)_2(en)(H_2O)]$ with H_2O_2 was mainly $[Cr(en)(H_2O)_4]^{3+}$ with minor amounts of $[Cr(H_2O)_6]^{3+}$; the products for the $[Cr(O_2)_2(dien)]$ reaction were not identified.

The reduction of $[Cr(O_2)_2(dien)]$ by a number of substrates has been investigated by Gould and coworkers. Chromium(III) and dioxygen are the final products when hydroxylamine,[60] ascorbic acid,[61,62] and mercaptocarboxylic acids[63] are the reductants. The reactions appear to proceed via Cr^{III}–$O^\bullet$ intermediates and are catalyzed by $Fe^{II,III}$ and in some cases Cu^{II} and $V^{IV,V}$. Faster reductions by the one-electron reductants Ti^{III} and $Fe(CN)_6^{4-}$ also yield Cr^{III} and O_2, but VO^{2+} reduces chromium only, releasing free peroxide.[64]

D. 1:1 Complexes

A few 1:1 complexes of dioxygen and chromium have been reported. Among these are the only chromium–dioxygen complexes that appear to exhibit end-on coordination of O_2. No X-ray crystal structure analyses have yet been reported for this group of chromium compounds.

The reaction of Cr^{II} and dioxygen in aqueous solution has been found (using pulse radiolysis) to produce a 1:1 complex as a first step.[65,66] More recently Espenson and co-workers have studied the reactions and decomposition of this complex, formulated as $[(H_2O)_5Cr(O_2)]^{2+}$, the aqueous superoxochromium(III) cation. It is also produced by the reaction of H_2O_2 with pentaaquaoxochromium(IV), $[(H_2O)_5CrO]^{2+}$.[67] Although superoxochromium(III) has not been isolated, chemical and spectroscopic[68,69] as well as theoretical[70] evidence favors an η^1-bonded O_2 configuration for the complex. It is not very stable and is generally produced at a concentration of 10^{-4} M or less. It decomposes[68] unimolecularly

$$Cr^{2+} + O_2 \rightleftarrows [Cr(O_2)]^{2+}$$

reacts with itself

$$2[Cr(O_2)]^{2+} + 4H_2O \rightarrow 2HCrO_4^- + 6H^+$$

and with Cr^{2+}

$$[Cr(O_2)]^{2+} + 3Cr^{2+} + 2H_2O \rightarrow 2[Cr_2(OH)_2]^{4+}$$

The kinetics of the reactions of $[Cr(O_2)]^{2+}$ with $N_2H_5^+$,[71] various transition metal complexes,[72] and (hydroxymethyl)chromium(III)[73] have been studied.

One-electron reduction of $[Cr(O_2)]^{2+}$ with outer-sphere reductants such as $[Rh(NH_3)_6]^{2+}$ results in $CrOOH^{2+}$, the hydroperoxochromium(III) cation.[69,73] This species is implicated as an intermediate in the autoxidation of (hydroxymethyl)chromium(III) using $[Cr(O_2)]^{2+}$ as a catalyst.[73] The reduction of $CrOOH^{2+}$ by Fe^{2+} appears to proceed via a Fenton mechanism.[69]

Three chromium porphyrin complexes of dioxygen have been reported. The first was $[Cr(O_2)(tpp)(py)]$,[74] made by the irreversible reaction of dioxygen with the solid chromium(II) complex [Cr(tpp)(py)]. The magnetic moment of 2.7 μ_B indicated two unpaired electrons in the dioxygen adduct. An IR band at 1142 cm^{-1} was assigned to ν(O–O) and the similarity of this band to those of related Co(II) complexes led to the suggestion that [Cr(O_2)(tpp)(py)] contains superoxide bound end-on to Cr^{III}. This view implies coupling between an unpaired electron on the chromium and the single unpaired electron of O_2^-.

Other chromium porphyrin complexes of dioxygen were made by reacting O_2^- with Cr^{III}(tpp)Cl in DMSO solution. The first product of this reaction is Cr^{III}(tpp)(O_2^-)Cl,[75] characterized by a UV–vis spectrum. But with a 6-fold excess of superoxide a compound identified as Cr^{IV}(tpp)(O_2^-)Cl is formed, apparently through one or two unidentified Cr^V intermediates.[76] The Cr^{IV} porphyrin complex was characterized by UV–vis and ESR spectra and was found to resemble free O_2^- in its reactivity.

An organometallic peroxo derivative of chromium has been reported. Blue $LiCr(O_2)(mes)_3(thf)_3$[77] is produced by the reaction of $Li_2Cr(mes)_4(thf)_4$ with dioxygen. The magnetic moment of 2.94 μ_B indicates two unpaired electrons while the reaction with base to form chromate and the reaction with acid to form H_2O_2 supports a O_2^{2-} (peroxo) formulation for the coordinated dioxygen group and the assignment of +4 for the oxidation state of chromium.

An example of reversible dioxygen binding by chromium was reported for a zeolite into which Cr^{II} has been introduced by ion exchange.[78] The blue-lilac anhydrous zeolite turned gray when exposed to dry O_2 at 760 Torr. The sample was reported to desorb O_2 and change back to blue-lilac when the O_2 pressure was reduced. The room temperature magnetic moment of the gray material (3.7 μ_B) indicated spin pairing between the Cr and O_2. It was proposed that the zeolite contained a Cr^{III}–O_2^- complex. Another example of a reversible chromium–oxygen complex was postulated from mass spectroscopic evidence in the reaction of bis(ethylbenzene)chromium with dioxygen.[79]

Photolysis of $Cr(CO)_6$ in an O_2-doped argon matrix at 10–20 K ultimately results in formation of CrO_2; a chromium–dioxygen complex was proposed as an intermediate.[80]

A series of three yellow compounds of proposed formula $[Cr(O)_2(O_2)L]$ has been reported[81] with L = dien, trien, and 2,3,2-tet (= $NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$). These were made by treating CrO_3 with 30% H_2O_2 and adding the resulting solution to an ethanolic solution of the base. The complexes were characterized by elemental analysis and IR spectra and were reported as undissociated in solution on the basis of molar conductance data. These compounds are the only Cr^{VI} monoperoxo complexes reported, and the method of synthesis is similar to that of some Cr^{IV} diperoxo compounds (see above). A definitive study such as an X-ray crystal structure analysis on one of these complexes would be desirable.

E. Other Complexes

The reaction of Cr^{VI} with H_2O_2 in acidic aqueous solution at temperatures lower than 0 °C results in green cationic species.[29] Two of these were tentatively identified as CrO_2Cr^{4+} and $CrO_2CrO_2Cr^{5+}$ on the basis of oxidizing capacity and rate of elution from ion-exchange columns. A third complex, assumed to be a tetramer, could not be eluted from the column. Production of such green species depends upon the concentration of Cr^{VI}; kinetic studies of the $Cr^{VI} + H_2O_2$ reaction (see section II.C.1) have apparently been conducted at Cr^{VI} concentrations too low to observe formation of the green species.[31]

Recently, the green dimeric species was shown to react with Cr^{2+} to produce an aquachromium(IV) complex.[82]

III. Molybdenum and Tungsten

It is convenient to discuss most of the dioxygen complexes of these two elements in parallel since there are many analogous and isostructural species. With the exception of some porphyrin derivatives, see sections III.C.3 and III.D.3, these complexes may be, and have been, regarded as peroxo species of the elements in oxidation state VI.

A. 4:1 Complexes

The anions $[M(O_2)_4]^{2-}$ (M = Mo, W) are formed in mildly alkaline solution (pH 7–9) by the addition of excess H_2O_2 to solutions of MO_4^{2-}. Several salts of mono- and divalent cations have been reported.[2] All are unstable and are prone to explode when struck or heated. The tetraperoxomolybdate anion is red, and the corresponding tungstate is yellow. The structures of $[Zn(NH_3)_4]_2[Mo(O_2)_4]$[83] and $K_2[W(O_2)_4]$[84] have been reported and reveal anions with the distorted dodecahedral (D_{2d}) geometry, on the basis of a tetrahedral arrangement of four η^2-O_2^{2-} ligands, as found for $[Cr(O_2)_4]^{3-}$ (Figure 1). Unlike the case for the d^1 Cr^V species, there are no significant differences in the metal–oxygen bond lengths for the tungstate and probably not, given the quality of the film data, for the molybdate. Infrared and Raman spectra have been reported for tungstate salts and solutions.[85] In the latter a polarized band at 858 cm^{-1} is assigned to ν(O–O). The molybdate species is too unstable to record a Raman spectrum, but a narrow signal at −426.5 ppm (*vs* MoO_4^{2-}) has been observed in the ^{95}Mo NMR spectrum.[85] Electronic structure calculations have been reported for the peroxomolybdate, using (1) an all-valence-electron self-consistent molecular orbital method, which is in reasonable agreement with the experimental electronic spectrum (shoulder at 44 000 cm^{-1})[86]; (2) an SCF-MS-Xα approach which reveals, in contrast to the peroxochromate, significant involvement of the peroxide σ(p) orbitals with the metal's 4d orbitals;[23] and (3) an INDO/1 calculation.[25] On the basis of O-18 studies, thermal decomposition of solid $K_2[W(O_2)_4]$ yields O_2 with 50% retention of the peroxide bond and decomposition in solution results in 80–100% retention, depending on pH.[87] Both molybdate and tungstate peroxoanions are unstable in solution at high pH (>9); below pH 5 they are progressively converted into the tetraperoxodimetalate anions discussed in section III.C. Thermal decomposition of aqueous solutions at pH 8.6–11.8 gives singlet oxygen in good yields.[88,89]

B. 3:1 Complexes

In molybdate–peroxide solutions at pH 8.4, polarized Raman bands at 959, 872, and 539 cm^{-1} have been

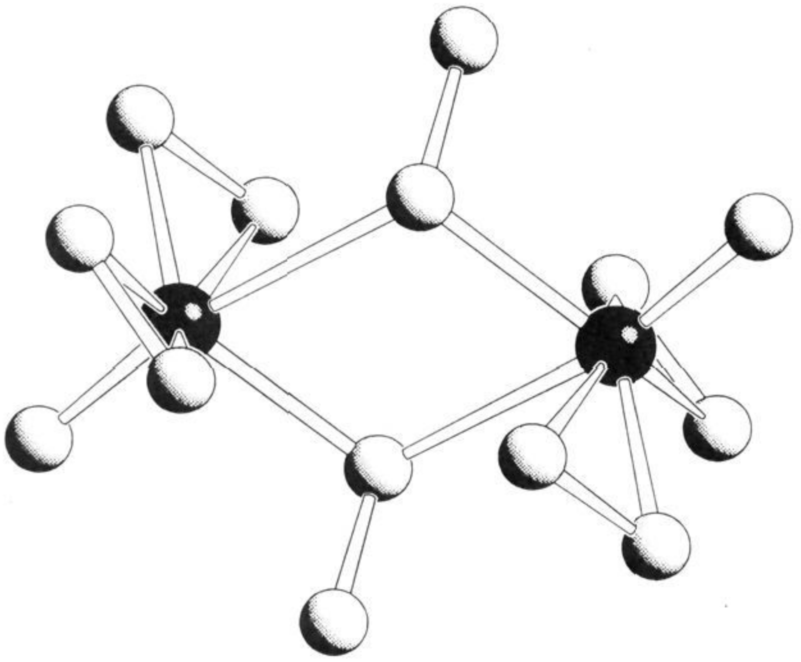

Figure 5. $[MoO(O_2)_2(OOH)]_2^{2-}$ (H atoms omitted from bridging OOH groups).

tentatively attributed to $[MoO(O_2)_3]^{2-}$, as has a narrow ^{95}Mo NMR signal at −492.3 ppm observed in solutions at pH 7.2 to 5.0.[85] The latter solutions also show a broader resonance at −266 ppm from $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ (see section III.C.1). Salts of triperoxoanions have been claimed, *e.g.* $Cs_2[MoO_7]$,[90,91] $K_2[WO_7]\cdot nH_2O$,[92] but there is no convincing evidence that these are pure species, and "$(Hpy)_2[MO_7]$" (M = Mo, W).[93] have been shown to be $(Hpy)_2[M_2O_3(O_2)_4(H_2O)_2]\cdot H_2O$.[94] The only confirmed "triperoxomolybdate" is the salt reported as $(Hpy)_2[Mo_2O_{11}]\cdot 2H_2O_2$[93] and later shown to contain bridging hydroperoxo ligands, $[MoO(O_2)_2(OOH)]_2^{2-}$.[95,96] As shown in Figure 5, the structure consists of a pair of edge-shared pentagonal bipyramids. Each hydroperoxo ligand occupies an axial position in one bipyramid and an equatorial position in the other with O–Mo distances of 2.39 and 2.04 Å, respectively. There is no significant difference between the O–O distances in the hydroperoxo (1.46 Å) and η^2-peroxo ligands (1.47 Å).

C. 2:1 Complexes

A large number of such complexes is known. In virtually all cases where the structures have been determined or inferred, the metal atoms are seven-coordinate, $[MO(O_2)_2L_{ax}L_{eq}]^{0/1-/2-}$ with a pentagonal bipyramidal geometry (*cf.* Figure 3). The oxo and one L ligand (or donor atom of a bidentate ligand) occupy axial positions, and the two η^2-peroxo groups and the remaining L are equatorial, see Table 3. Ligands L may also function as bridging groups in binuclear species, as seen in Figure 5 and summarized in Table 4. A few diperoxo complexes do not fit into this category and are discussed separately (section III.C.4).

1. Aqua Species

As the pH of peroxide-rich solutions of molybdate or tungstate is lowered the tetraperoxoanions are converted into dimers of diperoxo species

$$2[M(O_2)_4]^{2-} + 5H_2O \rightleftarrows [M_2O_3(O_2)_4(H_2O)_2]^{2-} + 2OH^- + 4H_2O_2 \quad (1)$$

It is believed that the same species are also formed when molybdenum and tungsten powders are dissolved in cold 30% H_2O_2.[97] Alkali metal salts of the diperoxo anions have been known for over 60 years, and early potentiometric and cryoscopic studies have confirmed the dimer formulation in solution. The anion structure is revealed in crystallographic investigations of $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$,[98] $(Hpy)_2[Mo_2O_3(O_2)_4(H_2O)_2]$,[96] $(C_3H_5N_2)_2[Mo_2O_3(O_2)_4(H_2O)_2]$,[99] and K_2-

Table 3. Structurally Characterized Oxodiperoxo Complexes of Molybdenum(VI) and Tungsten(VI), $[MO(O_2)_2L_{ax}L_{eq}]^{n-}$ (n = 0,1,2)

metal	L_{ax}	L_{eq}	n	ref(s)
Mo	H_2O	H_2O	0	*a*
Mo	H_2O	hmpt	0	*b*
W	H_2O	hmpt	0	*c*
Mo	py	hmpt	0	*b*
W	H_2O	(tacn)WO_3	0	*d*
Mo	$^1/_2$(dml[*ol*])	$^1/_2$(dml[*one*])	0	*e,f*
Mo	$^1/_2$(bipy)	$^1/_2$(bipy)	0	*g*
Mo	$^1/_2$(tbbpy)	$^1/_2$(tbbpy)	0	*h*
Mo	H_2O	Hgly	0	*i*
Mo	H_2O	Hpro	0	*i*
Mo	F^-	F^-	2−	*j,k*
Mo	$^1/_2$(ox)	$^1/_2$(ox)	2−	*l*
W	$^1/_2$(ox)	$^1/_2$(ox)	2−	*m*
Mo	$^1/_2$(glyc)	$^1/_2$(glyc)	2−	*n*
Mo	$^1/_2$(cit)	$^1/_2$(cit)	2−	*o*
Mo	$^1/_2$(pic[*N*])	$^1/_2$(pic[*O*])	1−	*p*

[a] Shoemaker, C. B.; Shoemaker, D. P.; McAfee, L. V.; DeKock, C. W. *Acta Crystallogr., Sect. C Cryst. Struct. Commun.* **1985**, *C41*, 347–50. [b] Le Carpentier, J. M.; Schlupp, R.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *28* (Pt. 4), 1278–88. [c] Amato, G.; Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G.; Valle, G. *J. Mol. Catal.* **1986**, *37*, 165–75. [d] Schreiber, P.; Wieghardt, K.; Nuber, B.; Weiss, J. *Z. Anorg. Allg. Chem.* **1990**, *587*, 174–92. [e] Kagan, H. B.; Mimoun, H.; Mark, C.; Schurig, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 485. [f] Winter, W.; Mark, C.; Schurig, V. *Inorg. Chem.* **1980**, *19*, 2045–8. [g] Schlemper, E. O.; Schrauzer, G. N.; Hughes, L. A. *Polyhedron* **1984**, *3*, 377–80. [h] Herrmann, W. A.; Thiel, W. R.; Kuchler, J. G.; Behm, J.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1963–70. [i] Djordjevic, C.; Vuletic, N.; Sinn, E. *Inorg. Chim. Acta* **1985**, *104*, L7–L9. [j] Stomberg, R. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 659–69. [k] Stomberg, R. *J. Alloys Comp.* **1992**, *186*, 271–8. [l] Djordjevic, C.; Covert, K. J.; Sinn, E. *Inorg. Chim. Acta* **1985**, *101*, L37–L39. [m] Stomberg, R.; Olson, S. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 79–83. [n] Dengel, A. C.; Griffith, W. P.; Powell, R. D.; Skapski, A. C. *J. Chem. Soc., Dalton Trans.* **1987**, 991–5. [o] Flanagan, J.; Griffith, W. P.; Skapski, A. C.; Wiggins, R. W. *Inorg. Chim. Acta* **1985**, *96*, L23–L24. [p] Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055–63.

Table 4. Structurally Characterized Dimeric Oxodiperoxo Complexes of Molybdenum(VI) and Tungsten(VI), $[MO(O_2)_2L_{ax}L_{eq}]_2^{2-}$

metal	L_{ax}	L_{eq}	ref(s)
Mo	H_2O	μ-O	*a–c*
W	H_2O	μ-O	*d*
Mo	$^1/_2$(μ-OOH)	$^1/_2$(μ-OOH)	*b*
Mo	$^1/_2$(μ-F^-)	F^-	*e*
W	$^1/_4$(μ_4-ox)	$^1/_4$(μ_4-ox)	*f*
Mo	$^1/_4$(μ_4-tart)	$^1/_4$(μ_4-tart)	*g*

[a] Stomberg, R. *Acta Chem. Scand.* **1968**, *22*, 1076–90. [b] Le Carpentier, J. M.; Mitschler, A.; Weiss, R. *Acta Crystallogr. Sect. B* **1972**, *28* (Pt. 4), 1288–98. [c] Djordjevic, C.; Gundersen, J. L.; Jacobs, B. A.; Sinn, E. *Polyhedron* **1989**, *8*, 541–3. [d] Einstein, F. W. B.; Penfold, B. R. *Acta Crystallogr.* (*Supplement*) **1963**, *16*, A35. [e] Stomberg, R. *J. Less-Common Met.* **1988**, *144*, 109–16. [f] Hashimoto, M.; Ozeki, T.; Ichida, H.; Sasaki, Y.; Matsumoto, K.; Kudo, T. *Chem. Lett.* **1987**, 1873–6. [g] Dengel, A. C.; Griffith, W. P.; Powell, R. D.; Skapski, A. C. *J. Chem. Soc., Chem. Commun.* **1986**, 555–6.

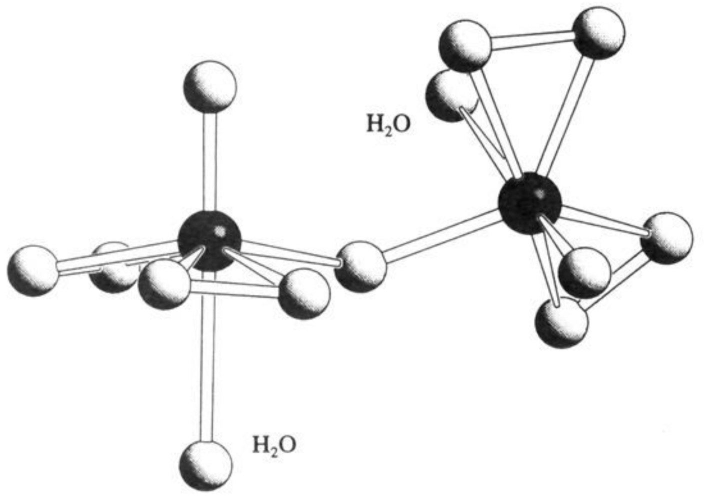

Figure 6. $[M_2O_3(O_2)_2(H_2O)_2]^{2-}$ (H atoms omitted).

$[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$[100] and may be described as two corner-linked pentagonal bipyramids each with apical oxo and aqua ligands (see Figure 6). The dimeric anions (δ ^{95}Mo, −266 ppm; δ ^{183}W, −699 ppm) are believed to be the species responsible for molybdate and tungstate catalysis of alcohol oxidation and alkene epoxidation by H_2O_2.[85] Organic solvent-soluble Ph_4P^+ and $Ph_3PhCH_2P^+$ salts of these species have been shown to be stoichiometric and catalytic oxidants/epoxidants in dichloromethane and dichloroethane.[85,101]

There is good evidence for the rapid formation of the monomeric species with large formation constants in dilute (*ca.* 0.1 mM) acidic solution (0.10–1.00 M H^+).[102,103] These are presumed to be $[MO(O_2)_2(H_2O)_2]$. Hydrolysis to $[MO(O_2)_2(OH)(H_2O)]^-$ is governed by pK_a's of 1.85 (Mo) and 0.1 (W), and dimerization is not apparent at concentrations below 0.04 M (Mo) and 0.02 M (W). The dimerization constant has been estimated at 0.0195 ± 0.05 M^{-1}.[104] Crystals containing the neutral monomeric molybdenum species were obtained adventitiously from an experiment in which MoO_3 and tetrahydrofuran were co-condensed in a metal vapor reactor at 77 K. The condensate was stirred with excess THF, exposed to air and light, and treated with a small amount of water and 18-crown-6, ultimately to yield yellow crystals of $[MoO(O_2)_2(H_2O)_2]\cdot C_{12}H_{24}O_6\cdot H_2O$.[105] The conditional formation constants (K_f = [complex]/$\{M(VI)\}[H_2O_2]^2\}$) for both molybdenum and tungsten species are of the order of 10^6 M^{-2} at pH 6.6–7.7 and increase rapidly as the pH is lowered.[106] Rates of complex formation and of their reduction by Fe(II), Eu(II), dithionite, and methyl viologen radical cation have been measured. Such substrates are believed to react by an inner-sphere, one-electron reduction of a peroxo ligand to give a hydroxyl radical intermediate. The hydroxyl radical oxidizes the remaining peroxo ligand to form a superoxo Mo(VI) or W(VI) intermediate, which is rapidly reduced to peroxide by the reductant. The rate enhancements for the peroxo complexes relative to hydrogen peroxide are substantial (60–13 000).[106]

2. Oxodiperoxo Species

a. Neutral and Monoanionic Species. In 1969 Mimoun *et al.*[107] reported an important class of molybdenum- and tungsten-peroxo complexes formed by the treatment of a solution of MO_3 in 30% H_2O_2 with organic bases. Such aqueous solutions contain $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$, and the organic complexes may also be directly precipitated from solutions of the dimers. A large number of apparently analogous complexes have since (and perhaps previously[108,109]) been reported. Ligands now include water, amides,[107] ureas,[107] phosphoramides,[107,110–114] amino acids,[115] pyridines,[107,114,116] pyridine *N*-oxides,[107,114,117] phosphine and arsine oxides,[107,117,118] and bidentate 2,2′-bipyridine,[107] 2,2′-bipyridine *N,N′*-dioxide,[97] picolinate and its *N*-oxide,[110,111,114,119,120] 1,10-phenanthroline,[118] phenylenediamine and ethanolamine,[121] octamethylpyrophosphoric triamide,[107] and (*S*)-dimethyllactamide.[122,123]

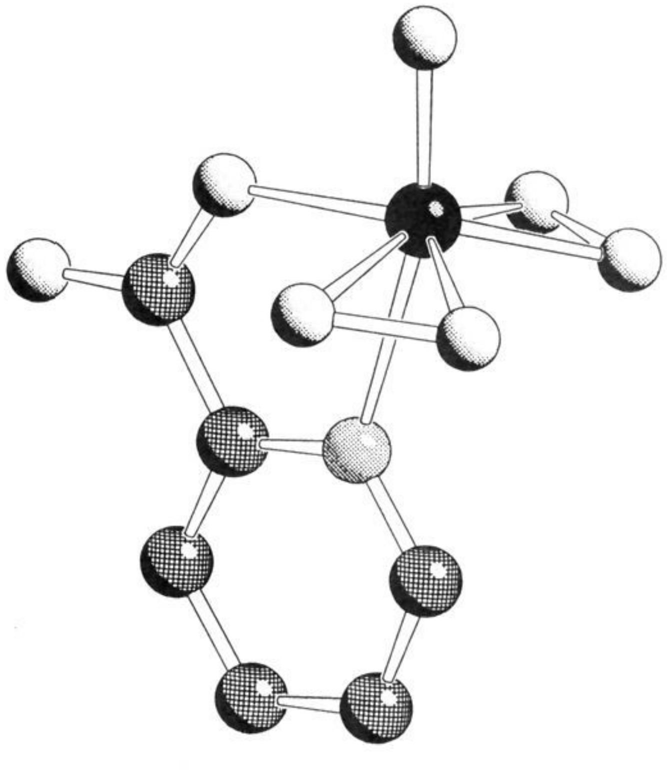

Figure 7. $[MoO(O_2)_2pic]^-$.

The molybdenum complexes are yellow and the tungsten complexes are white. Some of these complexes have been structurally characterized (see Table 3 and Figure 7), whereas others are merely reported with elemental analysis and IR data. The ^{17}O-NMR signal for the peroxo oxygens of MoO_5(hmpt) has been detected.[40] Since the neutral compounds and appropriate salts of the monoanions are readily soluble in both polar and nonpolar solvents these complexes have been widely used as both stoichiometric and catalytic oxidants in organic chemistry. Stoichiometric oxygen-transfer reactions include epoxidation of alkenes;[117,123–132] oxidation of primary and secondary alcohols to aldehydes and ketones respectively,[111,133,134] of epoxides to dioxetanes or fragmentation products,[135,136] of enolates and enol ethers to epoxides and dioxetanes,[45,137] of sulfides and sulfoxides to sulfoxides and sulfones,[138–140] indoles,[141,142] furans,[143] phenacetin,[144] organoboranes,[145,146] metal alkyls,[147,148] and organopalladium compounds.[149] In the majority of these investigations $[MoO(O_2)_2(hmpt)]$ has been the complex of choice, but other complexes are also effective. A mechanism in which the substrate first binds to the metal center and then inserts into the peroxo–metal bond, forming a metallocycle intermediate, was initially proposed,[124] but later investigations have favored direct attack of the substrate on a peroxidic oxygen.[125,130,138] Fewer investigations have been made with tungsten complexes, but studies indicate that $[WO(O_2)_2(hmpt)]$ is a more effective epoxidant than the molybdenum analogue[129,130] and, when differences in acidity are compensated for, has a greater catalytic efficiency for sulfide oxidations by H_2O_2.[150,151] Other diperoxo complexes have also been shown to be catalytically active in H_2O_2 oxidation of sulfides and epoxidation of alkenes.[101,152,153]

All of these reactions can be regarded as oxygen atom transfer processes, and proposed mechanisms for the stoichiometric epoxidations take into account the absence of oxygen exchange between oxo and peroxo ligands and the peroxo source of the atom transferred to the substrate.[124,125]

b. Monomeric and Dimeric Dianionic Complexes. *i. Fluoro Complexes.* The molybdate complex $[MoO(O_2)_2F_2]^{2-}$ has been isolated as potassium and ammonium salts,[154-156] and the structural determinations of ammonium salts[157,158] confirm the expected pentagonal-bipyramidal geometry. Other crystalline phases from the NH_4^+–MoO_4^{2-}–H_2O_2–HF–H_2O system include the monoperoxo complex (see section III.D) and two binuclear species $(NH_4)_3[\{MoOF(O_2)_2\}_2F]$ and $(NH_4)_3[\{MoO(O_2)_2\}_2FO]$ with μ-F and μ-F,O respectively.[158,159]

ii. Carboxylate Complexes. Dianionic complexes, $[MO(O_2)_2LL]^{2-}$ (M = Mo,W) with bidentate ligands LL = oxalate,[160-163] citrate, tartrate, malate, and glycolate,[162,164] and, for M = Mo, tartronate and quinate,[162] have been described and, in some cases (Table 3), structurally characterized. An electronic structure calculation has been made for the oxalatomolybdate.[86] Molybdenum-95 NMR chemical shifts for these complexes are ligand dependent: (in ppm *vs* MoO_4^{2-}) −228.3 (ox), −220.6 (glyc), −233.0 (mal), −247.0 (cit).[162] Unlike the neutral diperoxo complexes discussed in the previous section, the dianions were ineffective at epoxidation of alkenes.[162]

Dimeric complexes have been reported and structurally characterized. The structure of $[Mo_2O_2(O_2)_4(C_4H_2O_6)]^{4-}$ (and presumably of the analogous tungstate) contains bis-bidentate bridging tartrate(4−); the axial positions of the MoO_5 pentagonal bipyramids are occupied by carboxylate oxygens, and the equatorial positions by the deprotonated hydroxyl groups.[165] A similar coordination mode was observed in the (monomeric) $[MoO(O_2)_2(cit)]^{2-}$ complex.[164] The tartrato complex retains its dimeric structure in solution (δ ^{13}C, 89.0, 186; ^{95}Mo, −235) and does not epoxidize alkenes. Dissolution of tungsten carbide in H_2O_2 and subsequent workup of the product, yields non-peroxo polytungstates and $[W_2O_2(O_2)_4(C_2O_4)]^{2-}$, isolated as the tetra-*n*-butylammonium salt and structurally characterized.[166] As in the tartrato complex, oxalate(2−) functions as a bis-bidentate bridging ligand for the two $WO(O_2)_2$ moieties.

3. Porphyrin Derivatives

Several diperoxomolybdenum porphyrin complexes have been reported, and the structure of *trans*-diperoxomolybdenum tetraparatolylporphyrin (tptp) has been determined (Figure 8).[167] The stereochemistry of this complex, in which the mutually perpendicular peroxo ligands eclipse the equatorial Mo–N bonds, has been examined by LCAO-MO-SCF calculations.[168] Photolysis of the diperoxo complexes yields the *cis*-dioxomolybdenum porphyrin.[169,170] The corresponding complexes, *trans*-$[Mo(O_2)_2(por)]$ (por = tpp and 5,15-diphenyl-2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrinate), are similarly converted to *cis*-$[Mo(O)_2(por)]$ by photoirradiation[171] or by pyrolysis of the solid at 200 °C under 10^{-3} Torr.[172] Electrochemical investigations of *trans*-$[Mo(O_2)_2por]$ (por = tptp, tmtp) in dichloromethane reveal reversible one-electron oxidation and reduction processes. The products of electrolysis, $[Mo(O_2)_2por]^+$ and $[Mo(O_2)_2por]^-$, are both ESR active and contain radical–cation porphyrin and Mo^V, respectively. A subsequent reduction leads to unstable, ESR-silent Mo^{IV} species.[173,174]

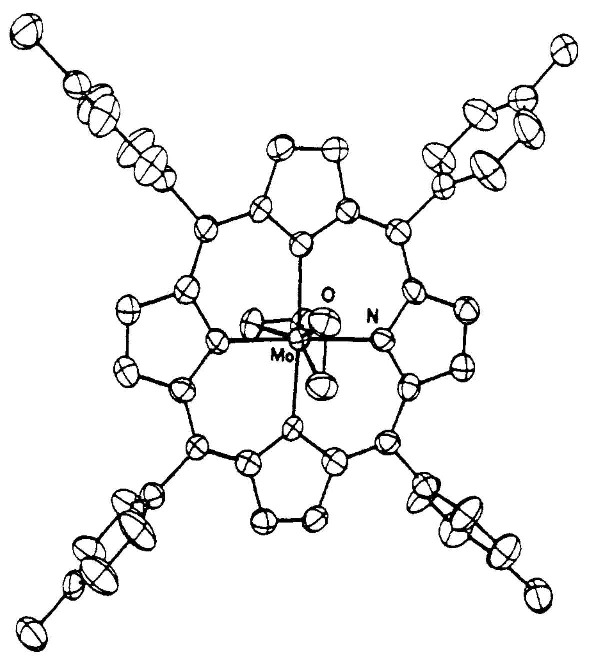

Figure 8. $[Mo(O_2)_2tptp]$.

4. Non-Oxo Diperoxo Species

In addition to the porphyrin species described above, neutral complexes $[ML_2(O_2)_2]$, M = Mo, W; L = *S*-benzyldithiocarbazate(−), have been reported and characterized by elemental analysis and IR spectroscopy.[175] The ligand is presumed to function in a bidentate (*N*,*S*) fashion. The complexes are inactive toward alkenes. The tungsten complex reacts further to yield 1:1 triphenylphosphine and triphenylarsine adducts.

D. 1:1 Complexes

1. $MO(O_2)L_4$-type Complexes

Oxomonoperoxo complexes of molybdenum and tungsten generally exhibit the pentagonal-bipyramidal geometry observed for the diperoxo species but with two equatorial ligands replacing one of the peroxo groups (see Figure 9 for example). Structurally characterized complexes are listed in Table 5. The tungsten analogue of the aqua–dipicolinato complex has been reported.[110,176] Other species which probably have similar structures contain various combinations of many of the ligands observed in the oxodiperoxo complexes described above.[121,177-182] The species $[MoO(O_2)(dipic)(hmpt)]$ reacts with anilines to yield $[MoO(\eta^2\text{-}ArNO)(dipic)(hmpt)]$ consistent with a mechanism involving attack of the nitrogen at the electrophilic peroxo oxygen.[181] Recently, complexes of stoichiometry $[MO(O_2)L^{(4)}]$, where $L^{(4)}$ is a quadridentate Schiff base, have been reported.[183,184] These, together with apparent dioxomonoperoxo complexes of molybdenum and tung-

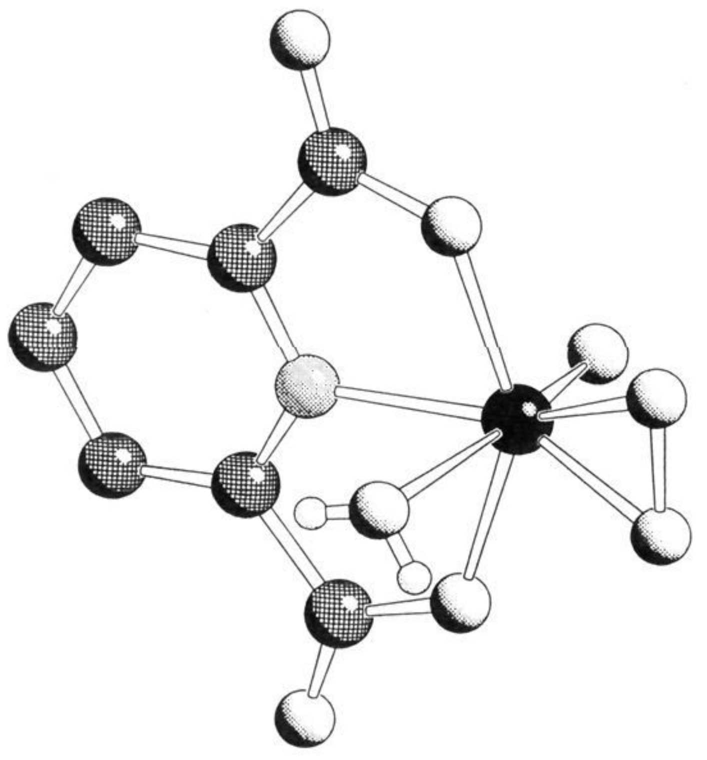

Figure 9. $[MoO(O_2)(H_2O)dipic]$.

Table 5. Structurally Characterized Oxomonoperoxo Complexes $[MO(O_2)L_{ax}(L_{eq})_3]^{n-}$

M	L_{ax}	L_{eq}	$n-$	ref(s)
Mo	F^-	F^-	2−	*a,b*
W	F^-	F^-	2−	*b*
Mo	CN^-	CN^-	2−	*c*
Mo	F^-	dipic(2−)	1−	*d*
Mo	Cl^-	pic(−), hmpt	0	*e*
Mo	H_2O	dipic(2−)	0	*f*

[a] Larking, I.; Stomberg, R. *Acta Chem. Scand.* **1970**, *24*, 2043–54. [b] Stomberg, R. *Acta Chem. Scand., Ser. A* **1988**, *A42*, 284–91. [c] Arzoumanian, H.; Lai, R.; Lopez Alvarez, R.; Petrignani, J. F.; Metzger, J.; Fuhrhop, J. *J. Am. Chem. Soc.* **1980**, *102*, 845–7. [d] Edwards, A. J.; Slim, D. R.; Guerchais, J. E.; Kergoat, R. *J. Chem. Soc., Dalton Trans.* **1977**, 1966–8. [e] Chaumette, P.; Mimoun, H.; Saussine, L.; Fischer, J.; Mitschler, A. *J. Organomet. Chem.* **1983**, *250*, 291–310. [f] Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055–63.

sten with tetradentate amine ligands, $[M(O)_2(O_2)L]$,[81] require more complete characterization.

Two dimeric species have been characterized structurally; the crystal complex $[F\{MoO(O_2)(dipic)\}_2]$ with bridging axial F^-,[185] and $[MoO(O_2)(C_3H_6O_2)(MeOH)]_2$,[186] which contains an *anti* conformation of $MoO(O_2)$-(MeOH) moieties bridged by an enantiomeric pair of 1,2-propanediolate(2−) ligands.

2. Cyclopentadienyl Complexes

Complexes of formula $[Cp'MO(O_2)R]$ ($Cp' = Cp, Cp^*$; $R = Me, CH_2SiMe_3$) were reported almost simultaneously by two research groups;[187,188] derivatives with R = Cl were described later.[189] These complexes are prepared by treatment of the dioxo species, $[Cp'M(O)_2R]$, with H_2O_2 in ether. Structures of both Cp and Cp* derivatives of $[Cp'WO(O_2)CH_2SiMe_3]$ (see Figure 10)[187,188] and NMR and IR data have been reported.[190,191] Formation of the peroxo species was shown to proceed without scission of the O–O bond of H_2O_2, and treatment of $[Cp^*MoO(O_2)Cl]$ with $H_2{}^{18}O$ leads to incorporation of the label into the oxo group only.[189] The molybdenum and tungsten alkyl complexes react with H_2S in CS_2 solution to yield the oxopersulfido species, $[Cp^*MO(\eta^2\text{-}S_2)R]$.[192]

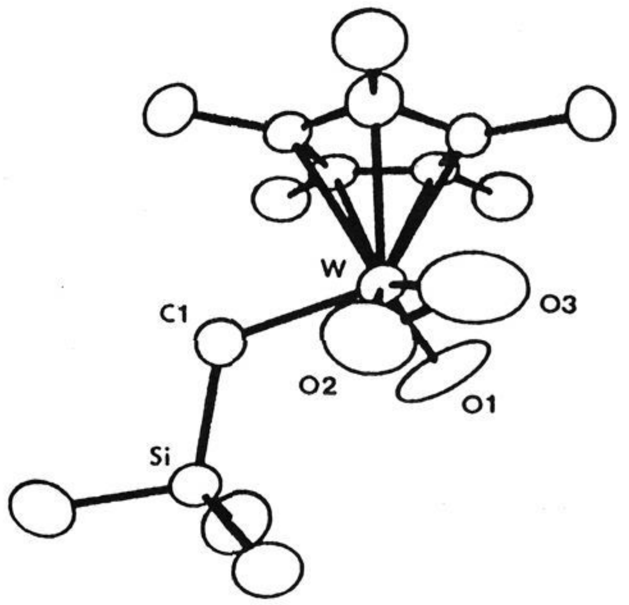

Figure 10. $[Cp'WO(O_2)CH_2SiMe_3]$.

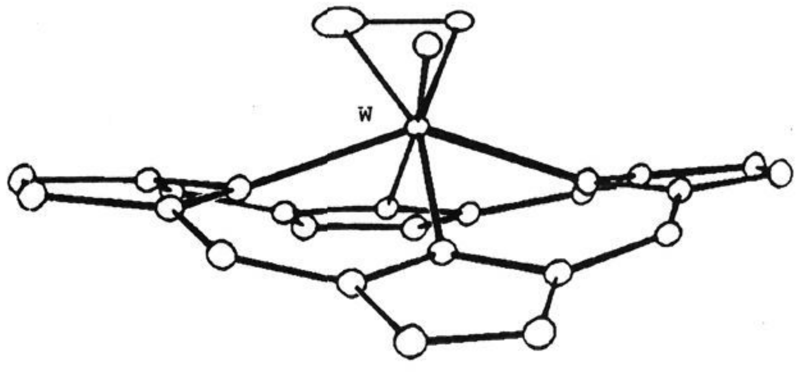

Figure 11. $[WO(O_2)tpp]$.

3. Porphyrin Derivatives

Apart from the curious *cis*-oxoperoxotungsten species, $[WO(O_2)tpp]$, shown in Figure 11,[193] most activity has concerned molybdenum porphyrin derivatives. The tungsten complex, with a large displacement (1.49 Å) of the metal atom from a porphyrin ring distorted into a double saddle shape, may formally be compared with the oxoperoxo complexes described in section III.D.1. Reaction with triphenylphosphine yields the *cis*-dioxo complex. In aprotic solvents the complexes $[Mo^{V}O(tpp)X]$ react with superoxide ion to yield $[Mo^{IV}O(tpp)]$. At −80 °C with excess superoxide an intermediate identified as $[Mo^{V}O(tpp)(O_2)]^-$ is generated and has been isolated as the potassium(18-crown-6) salt.[194,195] The new complex is ESR silent in solution at −80 °C (attributed to unfavorable spin relaxation), but yields a molybdenum ESR signal ($g = 1.97$) upon warming to −20 °C. A frozen solution of the potassium salt at −150 °C exhibits a rhombic ESR spectrum, from which it is concluded that the complex contains $\eta^2\text{-}O_2{}^{2-}$ *trans* to the oxo group. An earlier spectroscopic investigation[196] had indicated that neutral, ESR-active $[Mo^{V}O(tpp)(O_2)]$ resulted from the reaction of superoxide with $[Mo^{V}O(tpp)Br]$ in dichloromethane at room temperature, but this now appears to be erroneous. More recently, toluene solutions of $[Mo^{IV}O(tpp)]$ and $[Mo^{IV}O(oep)]$ have been shown to react reversibly with dioxygen at *ca.* −70 °C. Since pyridine blocks this reaction, forming $[MoO(tpp)(py)]$, it was concluded that the O_2 adduct (ESR silent at −70 °C) was *trans*-$[Mo^{VI}O(tpp)(\eta^2\text{-}O_2)]$.[197] Another dioxygen adduct of $[Mo^{IV}O(tpp)]$ has been formed by saturating a benzene solution of the porphyrin with O_2 at room temperature. Rapid quenching yields a solution with a triplet state ESR spectrum at 77 K. If the solution is allowed to stand in the dark, crystals of the μ-oxo face-to-face dimer, $[\{OMo^V(tpp)\}_2O]$, are formed. On the basis of an analysis of the ESR zero-field splitting parameters, it was concluded that the O_2 adduct was $[\{OMo^V(tpp)\}_2O_2]$ with μ-η^2-O_2^{2-}.[198] The water-soluble porphyrin derivative $[Mo^VO(tmpyp)OH]I_4$, where H_2tmpyp is the N-methylated version of tetrapyridylporphyrin, undergoes reaction with aqueous H_2O_2 to yield three different peroxo derivatives, depending upon pH. In acidic solutions (pH 1–3) the product was suggested to be $[Mo^{VI}(O_2)(tmpyp)(OH_2)]^{6+}$; at pH 3–5, $[Mo^{VI}(O_2)_2(tmpyp)]^{4+}$, and at pH 5–7.6, $[Mo^VO(O_2)(tmpyp)]^{3+}$ are said to be produced. The last complex is ESR active at room temperature.[199,200]

An alleged peroxomolybdenum(IV) porphyrin, $[Mo(O_2)(tpp)]$, is said to undergo photolytic conversion to $[Mo^{IV}O(tpp)]$.[201] No other reports of such a peroxo species have appeared before or since, and the source of this compound and proof of its composition were not given. The material originally reported to be "$[Mo^VO(tpp)OOH]$"[202,203] was shown to be a mixture of $[\{(MoO(tpp)\}_2O]$ and $[MoO(tpp)OEt]$.[204]

4. Cyano Derivatives

The bimetallic complex, $[(CN)_5Co^{III}O_2Mo^{VI}(O)Cl(CN)_5]^{6-}$, was isolated as a green potassium salt following passage of O_2 through an aqueous solution that contained $CoCl_2$, KCN, and $MoCl_5$.[205] If $MoCl_5$ was omitted, the same treatment yielded $[(CN)_5CoO_2Co(CN)_5]^{6-}$, and if $CoCl_2$ was omitted, the product was $[\{(CN)_5Mo^V(O)Cl\}_2O]^{8-}$. Treatment of an aqueous of the peroxo derivative with PPN^+Cl^- yields a blue species with no chloride and formulated as $(PPN)_5[(CN)_5CoO_2Mo(O)H_2O(CN)_5]$. Thermal treatment of the solid salt appears to result in the reversible loss of dioxygen. In organic solvents the bimetallic peroxo complex yields crystals of $(PPN)_2[MoO(O_2)(CN)_4]$ (confirmed by X-ray analysis) in a few hours at −15 °C.[206] The same compound could be obtained by treatment of $[\{(CN)_5Mo^V(O)Cl\}_2O]^{8-}$ in dichloromethane at −40 °C with Na_2O_2. The first direct observation of the ^{17}O NMR signal ($\delta = 487$) of transition metal-bound peroxo groups was made on this compound.[207]

High intensity photolysis of aqueous or aqueous–methanolic solutions of $[W^V(CN)_8]^{3-}$ is reported to yield $[(CN)_7WO_2]^{3-}$ and $[(CN)_7WO_2W(CN)_7]^{6-}$, identified by electronic absorption and Raman spectra. The dimeric species was isolated as a cadmium salt.[208] Both complexes were formulated as W^{IV} species with neutral dioxygen ligands, on the basis of Raman bands at 1345 and 1400 cm^{-1}. The complexes were considered to result from the reaction of superoxide ion (produced from photolytically generated $^\bullet OH$) with $[W^V(CN)_7(H_2O)]^{2-}$. A later investigation[209] of the same system identifies a narrow ESR line at $g = 1.9914$ with $[W^V(CN)_7OO^\bullet]^{2-}$, i.e. the W^V analogue of the previously claimed species. If confirmed, these could be the first examples of η^1-dioxygen binding to tungsten.

A yellow microcrystalline solid formed by dissolution of molybdenum metal in cold 30% H_2O_2 has been examined by IR and UV–reflectance spectroscopy, thermal analysis, and X-ray powder diffraction and tentatively identified as $MoO_2(O_2)\cdot H_2O$.[210,211]

Table 6. Structurally Characterized Peroxopolyoxoanions

formula	pH[a]	ref(s)
$[Mo_3O_7(O_2)_4]^{4-}$	8.3–9.2	*c*
$[Mo_4O_{12}(O_2)_2]^{4-}$	7–8	*d*
$[Mo_5O_{10}(O_2)_8]^{6-}$	8.1	*e*
$[Mo_7O_{22}(O_2)_2]^{6-}$	4–7	*f,g*
$[Mo_7O_{21}(O_2)_2(OH)]^{5-}$	3.0–5.3	*c*
$[Mo_8O_{24}(O_2)_2(H_2O)_2]^{4-}$	1.5–2.8	*c*
$[Mo_{10}O_{22}(O_2)_{12}]^{8-}$	2.8–3.0	*h*
$[W_4O_8(O_2)_6(CO_3)]^{6-}$	10	*i*
$[H_2W_6O_{15}(O_2)_4(SO_4)_2]^{4-}$	<1	*j*
$[W_4O_4(O_2)_8(PO_4)]^{3-}$	*b*	*k*
β_3-$[(CoO_4)W_{11}O_{31}(O_2)_4]^{10-}$	5	*l*

[a] pH of solution from which anion was crystallized. [b] Isolated as a tetra-*n*-hexylammonium salt from a biphasic medium. [c] Trysberg, L.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1981**, *A35*, 823–5. [d] Stomberg, R.; Trysberg, L.; Larking, I. *Acta Chem. Scand.* **1970**, *24*, 2678–9. [e] Persdotter, I.; Trysberg, L.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 1–7. [f] Larking, I.; Stomberg, R. *Acta Chem. Scand.* **1972**, *126*, 3708–22. [g] Persdotter, L.; Trysberg, L.; Stomberg, R. *Acta Chem. Scand. Ser. A* **1986**, *A40*, 335. [h] Persdotter, I.; Trysberg, L.; Stomberg, R. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 83–90. [i] Stomberg, R. *Acta Chem. Scand., Ser. A* **1985**, *A39*, 507–14. [j] Hashimoto, M.; Iwamoto, T.; Ichida, H.; Sasaki, Y. *Polyhedron* **1991**, *10*, 649–51. [k] Venturello, C.; D'Aloisio, R.; Bart, J. C. J.; Ricci, M. *J. Mol. Catal.* **1985**, *32*, 107–10. [l] Bas-Serra, J.; Todorut, I.; Jameson, G. B.; Acerete, R.; Baker, L. C. W. *Abstracts of Papers*; Internat. Chem. Congr. Pacific Basin Soc., jointly sponsored and published by the Chemical Society of Japan, Chemical Institute of Canada, and the American Chemical Society, Honolulu, HI, 1989; INOR776.

E. Polyoxometalate Derivatives

Molybdenum(VI) and tungsten(VI) form a enormous variety of polyoxoanions (isopoly and heteropoly species).[212-215] Addition of H_2O_2 to aqueous solutions of polyoxomolybdates and -tungstates generally leads to the formation of the simple monomeric or dimeric complexes described in sections III.C.1 and III.C.2. However if the concentration of H_2O_2 is kept fairly low, polynuclear peroxo complexes can be isolated. Much systematic structural investigation of peroxopolymolybdates has been carried out by Stomberg. Fewer polytungstate derivatives have so far been investigated. Structurally characterized species are summarized in Table 6. The molybdates listed in Table 6 may be regarded as *iso*polyperoxoanions. *Peroxide-rich* (O_2^{2-}/Mo > 1) structures are based on the *bis*(diperoxo)-molybdenum dimer (Figure 6). Thus $[Mo_3O_7(O_2)_4]^{4-}$ and $Mo_5O_{10}(O_2)_8]^{6-}$ contain μ-$OMoO_3^{2-}$ and μ_4-MoO_4^{2-}, respectively, in place of the aqua ligands of the dimer units (see Figures 12 and 13). The anion $[Mo_{10}O_{22}(O_2)_{12}]^{8-}$, has a structure based on eight $MoO_5(O_2)$ and two $MoO_3(O_2)_2$ pentagonal bipyramids (Figure 14) linked through bridging oxo and peroxo groups. Two kinds of bridging peroxo ligands are observed in this complex, the normal μ_2 mode (η^2:η^1), and an unusual μ_3 arrangement in which both oxygen atoms of an η^2-O_2^{2-} ligand bind to different molybdenum atoms. *Peroxide-poor* (O_2^{2-}/Mo < 1) species are related to known polyoxomolybdates with substitution of bridging oxo by peroxo ligands. Thus $[Mo_7O_{22}(O_2)_2]^{6-}$ (Figure 15) and $[Mo_8O_{24}(O_2)_2(H_2O)_2]^{4-}$ are based on heptamolybdate ($[Mo_7O_{24}]^{6-}$) and octamolybdate ($[Mo_8O_{28}]^{8-}$) frameworks, and $[Mo_4O_{12}(O_2)_2]^{4-}$ (Figure 16) is analogous to $[Mo_4O_{12}(OH)\{(CH_3)_2AsO_2\}]^{2-}$.[216]

Of the four tungstate complexes that are listed in Table 6, only one has a structure related to known

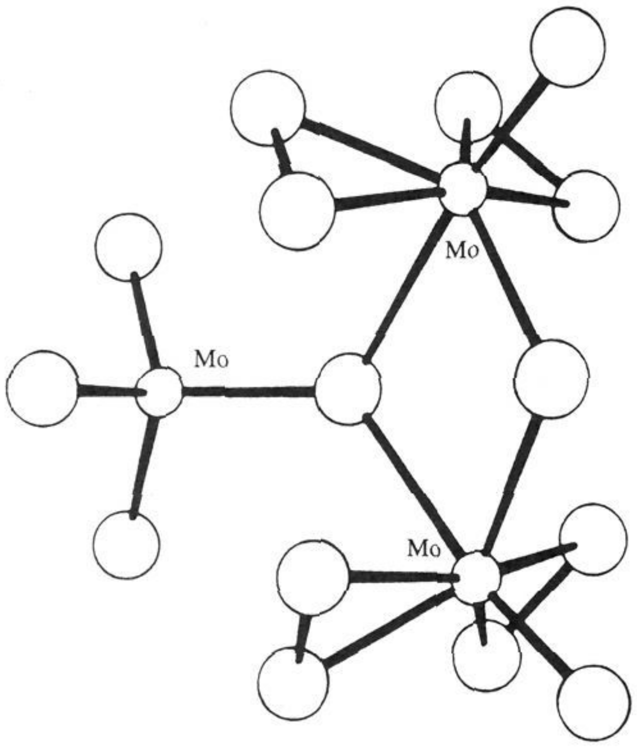

Figure 12. $[Mo_3O_7(O_2)_4]^{4-}$.

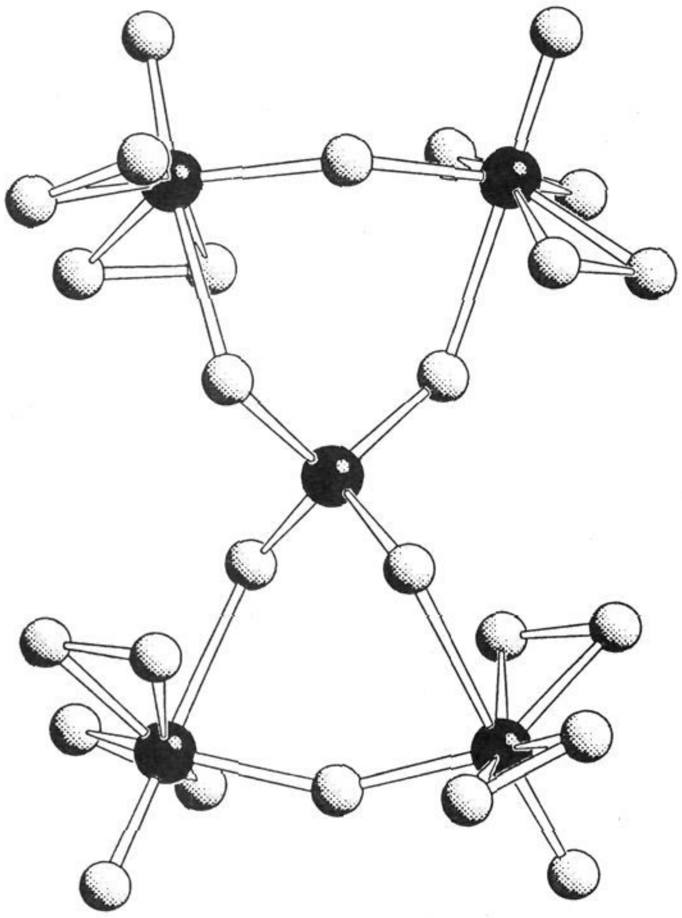

Figure 13. $[Mo_5O_{10}(O_2)_8]^{6-}$.

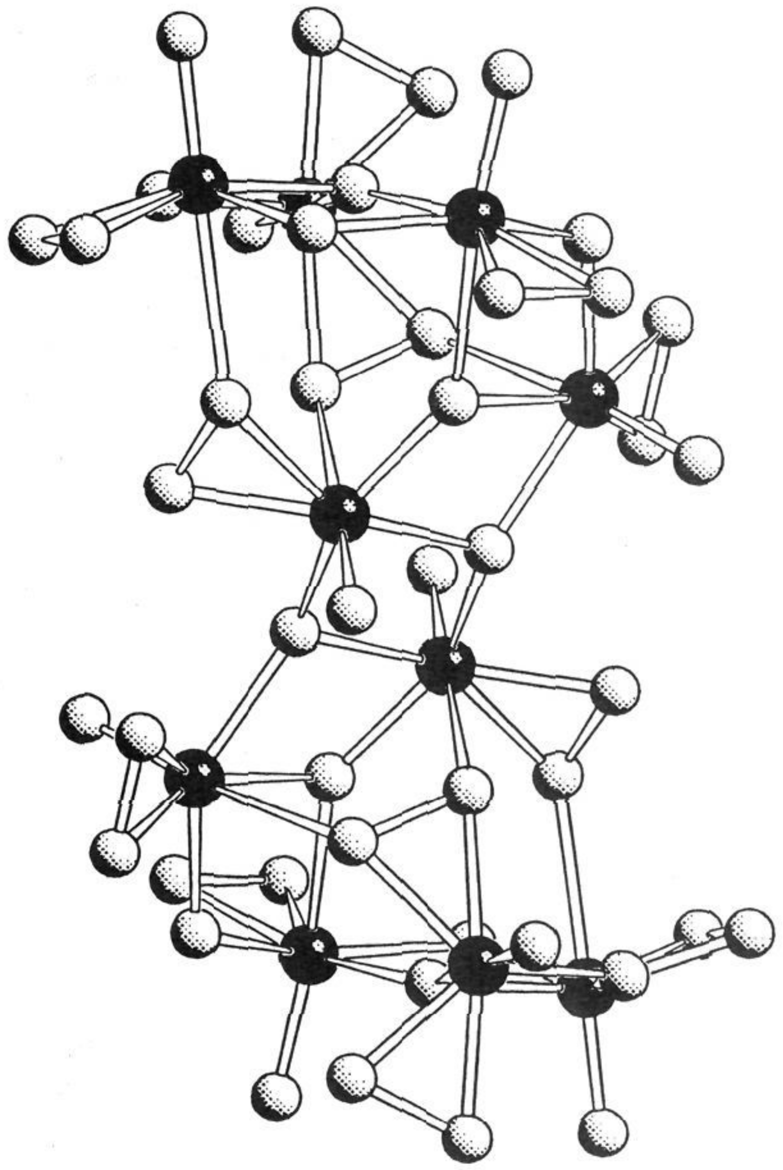

Figure 14. $[Mo_{10}O_{22}(O_2)_{12}]^{8-}$.

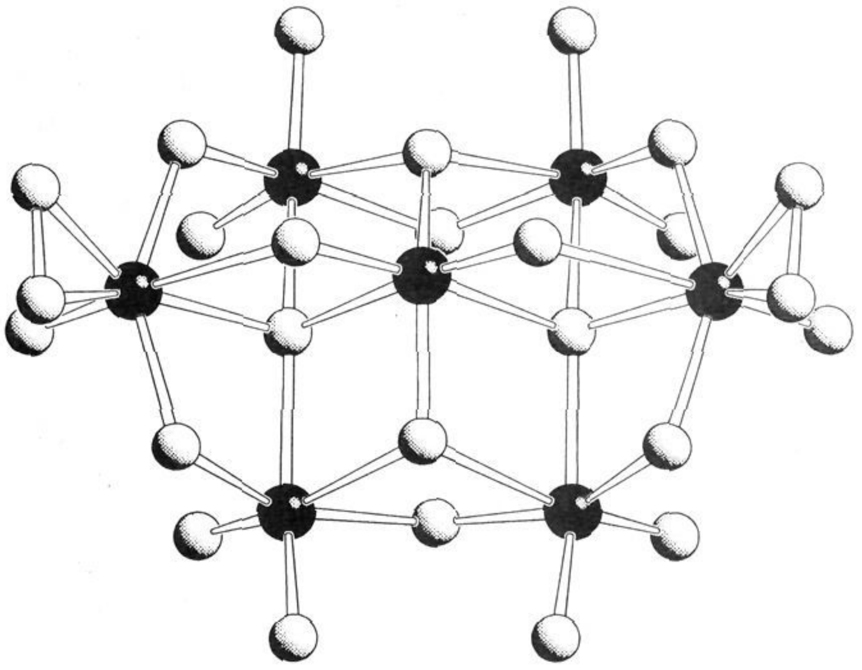

Figure 15. $[Mo_7O_{22}(O_2)_2]^{6-}$.

polyoxotungstates. Reduction of the lacunary tungstocobaltate(III) anion, α-$[(CoO_4)W_{11}O_{35}]^{9-}$, with H_2O_2 leads to a complex that has a fundamentally similar structure, but is one in which four tungsten atoms have been peroxidized (*cis*-$\{W(O)_2\}$ groups converted to $\{W(O)(O_2)\}$) (see Figure 17). Structures of the other three peroxopolytungstates are illustrated in Figures 18–20. The carbonato complex, $K_6[W_4O_8(O_2)_6(CO_3)]\cdot 6H_2O$ (Figure 18), isolated as colorless needles at pH 9, contains two diperoxo and two monoperoxo tungsten centers. The sulfato complex, $(N(CH_3)_4)_4[H_2W_6O_{15}(O_2)_4(SO_4)_2]$, (Figure 19) is isolated from a broad solution composition range at pH < 1 and contains four monoperoxo tungsten centers. No reactivity studies have been reported for these complexes.

The tungstophosphate anion, $[(PO_4)W_4O_4(O_2)_8]^{3-}$ (Figure 20), has a structure with both terminal (η^2) and bridging (η^2:η^1) peroxo ligands.[217] This structure may be contrasted with that of the isopolymolybdate $[(MoO_4)Mo_4O_6(O_2)_8]^{6-}$ (which also has a central μ_4-XO_4 group, see Figure 13) in which all peroxo ligands are nonbridging. The tungstophosphate is an excellent epoxidation and oxidation catalyst[217,218] and has been shown to be produced, as is an analogous molybdophosphate, in a biphasic catalytic system involving 12-tungstophosphoric or 12-molybdophosphoric acids, H_2O_2, and cetylpyridinium chloride.[219–221] Arsenate analogues of the peroxotungstates and -molybdates have also been investigated.[222]

Apart from the tungstocobaltate complex (Figure 17), no peroxo derivatives of the ubiquitous Keggin structure of heteropolytungstates and -molybdates have been structurally confirmed, although the tetramethylammonium salt of an anion formulated as

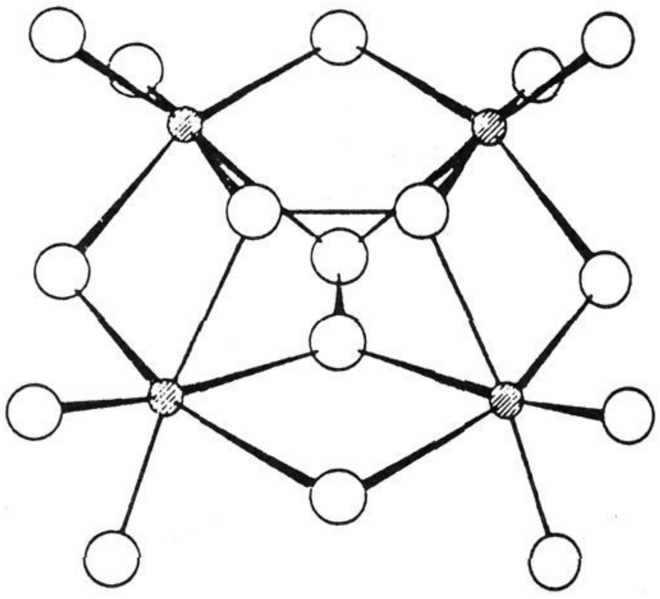

Figure 16. $[Mo_4O_{12}(O_2)_2]^{4-}$.

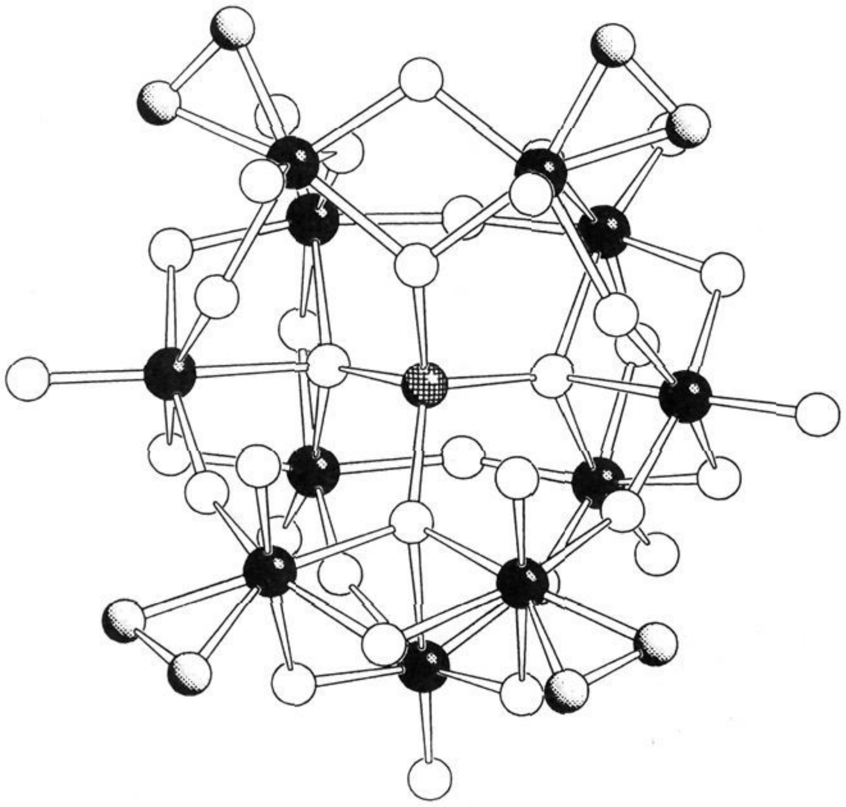

Figure 17. β_3-$[(Co^{II}O_4)W_{11}O_{31}(O_2)_4]^{10-}$. The η^2-peroxo ligands occupy positions *cis* to the terminal $W^{VI}{=}O$ bonds of the four tungsten atoms that surround the vacancy created by loss of WO^{4+} from β-$[(CoO_4)W_{12}O_{36}]^{6-}$ of C_{3v} symmetry.

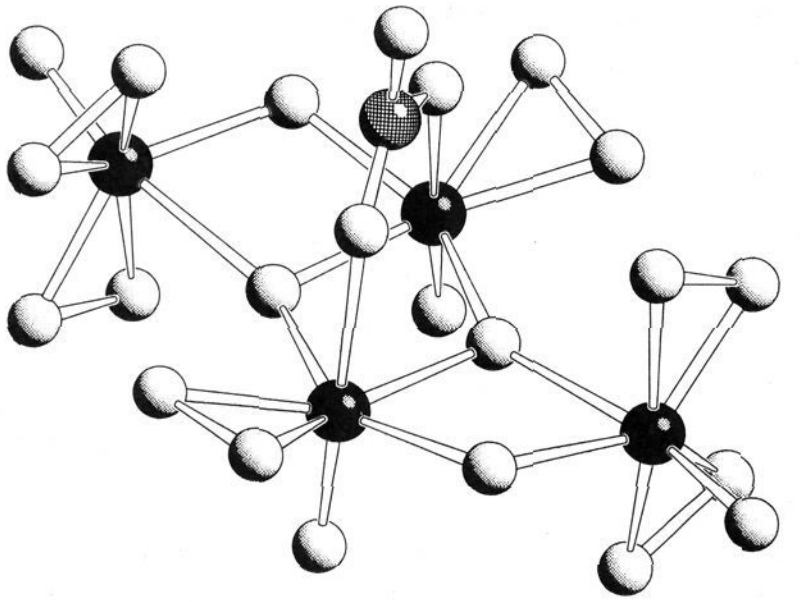

Figure 18. $[W_4O_8(O_2)_6(CO_3)]^{6-}$.

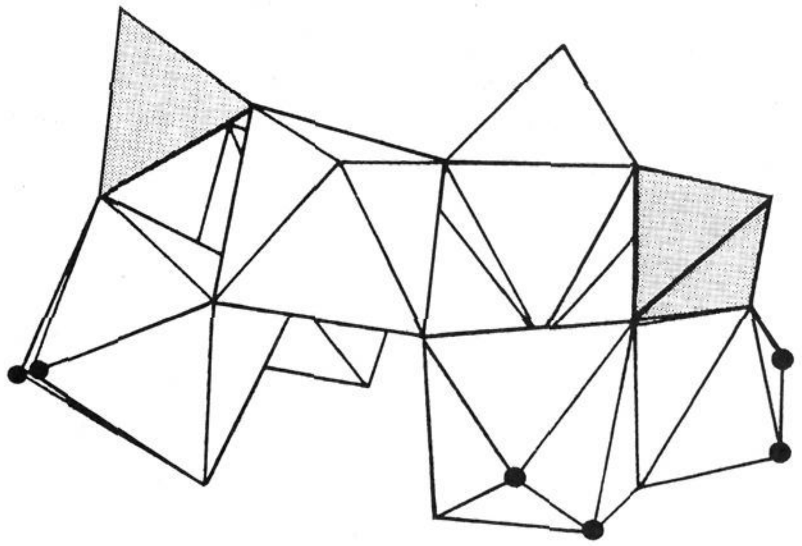

Figure 19. $[H_2W_6O_{15}(O_2)_4(SO_4)_2]^{4-}$ in polyhedral form, SO_4 tetrahedra shaded, peroxo oxygens indicated by dark circles.

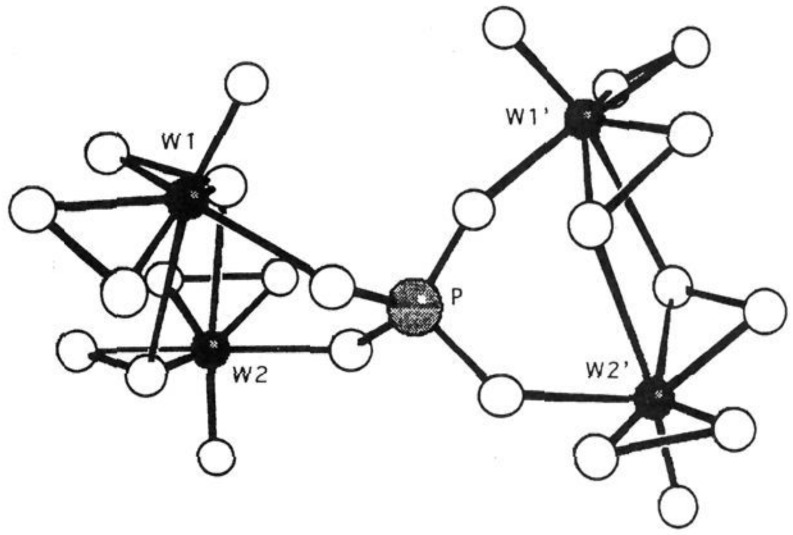

Figure 20. $[(PO_4)W_4O_4(O_2)_8]^{3-}$.

$[(H_2)W_{12}O_{39}(O_2)]^{6-}$ has been isolated. Infrared and ^1H NMR spectra are consistent with a Keggin structure with two central protons (*cf.* "metatungstate", $[(H_2)W_{12}O_{40}]^{6-}$). The anion undergoes an irreversible two-electron reduction at −0.32 V, pH 2.5, to yield the metatungstate anion, although the peroxo complex cannot be prepared directly from metatungstate.[223,224]

IV. Final Remarks

General patterns of structure and reactivity are now evident for the group 6 metal dioxygen complexes. The stereochemistry of the complexes in oxidation state VI can be understood when it is recognized that the η^2-O_2^{2-} ligand is a π-donor like the oxo ligand. Thus oxo and peroxo will always occupy mutually *cis* positions to interact with *different* metal ("t_{2g}") orbitals. The oxomonoperoxo complexes are therefore analogous to *cis*-dioxo species, and oxodiperoxo complexes are analogous to *fac*-trioxo species. The $\{M^{VI}O_5\}$ unit is observed for all three metals and is particularly prevalent in molybdenum chemistry. There is no reason to doubt that large numbers of WO_5 complexes can also be synthesized. These may prove to be as good as or, perhaps, better[130] than their molybdenum analogues at oxygen transfer activity. Unlike the dioxygen complexes of the later transition elements, these d^0 complexes are unambiguously peroxidic, with enhanced electrophilic character of the peroxo oxygens.[147] Redox potentials for Mo and W determine that virtually all of the peroxo complexes contain M^{VI}. In contrast, chromium forms complexes in oxidation states ranging from VI to III. It is curious that for the tetraperoxo complexes, $[M(O_2)_4]^{n-}$, M is hexavalent for Mo and W, but pentavalent for Cr. One possible rationalization is that Cr^{VI} might be too small to accommodate four η^2-O_2^{2-} ligands. The Cr^{IV} peroxo complexes have no analogues in Mo and W chemistry due presumably to unfavorable redox potentials. Two relatively recent and significant developments are the recognition of Cr^{III}–dioxygen species, to which the metastable superoxochromium(III) cation[67] provides an entree, and the multiperoxo polyoxoanions typified by $[(PO_4)W_4O_4(O_2)_8]^{3-}$.[217] The reactivity of the last species may result from the presence of pairs of bridging (η^1:η^2) peroxo ligands. In view of the vast known range of poly*oxo*anions of Mo and W, future explorations of poly*oxoperoxo* species, some of which are known to incorporate a variety of bridging peroxo groups, are likely to be productive in the search for improved and more selective thermal and catalytic oxidants.

V. Abbreviations

bipy	2,2′-bipyridine
bipy-OO	2,2′-bipyridine *N,N*′-dioxide
bpys	2,2′-bipyridine-5-sulfonate(−)
cit	citrate(2−)
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
dien	diethylenetriamine
dipic	dipicolinate(2−), pyridine-2,5-dicarboxylate(2−)
dma	*N,N*′-dimethylacetamide
dmf	*N,N*′-dimethylformamide
dml	(*S*)-*N,N*′-dimethylacetamide
en	ethylenediamine
Et	ethyl
gly	glycinate(−)
glyc	glycolate(2−)
hept	hexaethylphosphoric triamide
hexamine	hexamethylenetetramine
hmpt	hexamethylphosphoric triamide
ibn	isobutylenediamine
mal	malate(2−)
4-Mepy-O	4-methylpyridine *N*-oxide
mes	mesitylene
nic	nicotinic acid, pyridine-3-carboxylic acid
oep	2,3,7,8,12,13,17,18-octaethylporphyrinate(2−)
omppt	octamethylpyrophosphoric triamide
ox	oxalate(2−)
phen	*o*-phenanthroline
pic	picolinate(−), pyridine-2-carboxylate(−)
pic-O	pyridine-2-carboxylate(−) *N*-oxide
pn	propylenediamine
PPN	bis(triphenylphosphine)iminium(+)
pro	prolinate(−)
py	pyridine
py-O	pyridine *N*-oxide
quin	quinate(2−)
tacn	triazacyclononane
tart	tartrate(2−)
tbbpy	*N*-*tert*-butyl-2,2′-bipyridine-5-sulfonamide
tbuao	tri-*n*-butylarsine oxide
tbupo	tri-*n*-butylphosphine oxide
tept	triethylphosphoric triamide
thf	tetrahydrofuran
$tmpypH_3$	5,10,15,20-tetrakis(4-*N*-methylpyridyl)porphyrin(4+)
tmu	tetramethylurea
tpao	triphenylarsine oxide
tpp	5,10,15,20-tetraphenylporphyrinate(2−)
tmtp	5,10,15,20-tetra-*m*-tolylporphyrinate(2−)
tptp	5,10,15,20-tetra-*p*-tolylporphyrinate(2−)
tppo	triphenylphosphine oxide
tprao	tri-*n*-propylarsine oxide
tprpo	tri-*n*-propylphosphine oxide
tron	tartronate(2−)

Acknowledgments. Many of the figures were generated by SCHAKAL 92 (copyright Egbert Keller, Freiburg University) and are based on crystal atomic coordinates; we thank Professor L. C. W. Baker for providing the coordinates for $[(CoO_4)W_{11}O_{31}(O_2)_4]^{9-}$ from the Doctoral Dissertation of J. Bas-Serra, University of Valencia, 1989. We also acknowledge research support from the National Science Foundation and ARCO Chemical Co.

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