PERSPECTIVE

Vanadium and molybdenum peroxides: synthesis and catalytic activity in oxidation reactions

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Catalysis by transition metal ions in oxidation reactions with hydrogen peroxide and alkyl hydroperoxides is a leading topic in the pursuit of more sustainable and selective processes, to obtain compounds with high added value. The most recent achievements concerning the synthesis and characterization, as well as the key aspects of reactivity, of V(v) and Mo(vi) peroxo complexes have been collected here.

Introduction

The oxidative functionalization of organic and inorganic substrates is frequently obtained with peroxides, in mild conditions, in high yields and remarkable selectivity.[1–3] Originally, organic peracids, hydrogen peroxide and alkyl hydroperoxides were tested; however, it resulted that only with peracids were synthetically interesting procedures available because of their much higher

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reactivity in comparison with that of H_2O_2, *t*-butyl hydroperoxide or other simple peroxidic species.[2,3]

Notably, from the applied point of view, hydrogen peroxide is the most interesting one in consideration of its high oxygen content as well as its sustainability.[4] Unfortunately, being a weak oxidant, in order to be truly attractive, it needs to be activated. To this aim, the most effective catalysts, not considering strong bases or Brønsted acids, are some of the transition metal ions, above all those from groups 4–7, *i.e.* Ti, V, Cr, Mo, W and Re, in their highest oxidation states. The discovery of the catalytic activity of some of these metals in oxidation reactions with H_2O_2 was made early in the first half of the last century.[5] Later, it was demonstrated[6] that

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similar reactivity is observed also when alkyl hydroperoxides are used as the primary oxidants.

An extraordinary step forward in this field was obtained by Katsuki and Sharpless[7] in 1980 (in 2001 such a discovery was credited with the Nobel Prize), when the titanium catalysed enantioselective oxidation of prochiral allylic alcohols with alkyl hydroperoxides was realized, in the presence of chiral non racemic tartrates.

Studies in this field have been dedicated both to the applicability of such species as oxidants of numerous substrates, as well as to the elucidation of the mechanistic details of the oxidative process. The catalytic effect of the metal ions can be described in a very simple way as indicated in Scheme 1. The nature of the real oxidant depends on the peroxide used and on its interaction with the metal precursor, high-valent peroxometal species usually being the active intermediates.[3,8]
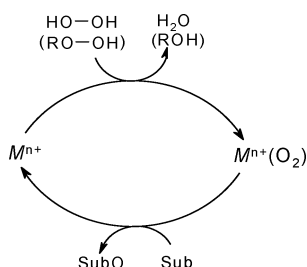
Scheme 1 Metal catalysed oxidations with peroxide.

As already anticipated, the reactivity of the peroxo† and/or peroxide metal complexes is orders of magnitude higher than that of the peroxidic precursor, either H_2O_2 or ROOH.

The elucidation of the essential steps in the metal catalyzed oxidations with peroxides, directed research interests towards the understanding of the structure, in solid state as well as in solution, and the chemical behaviour of peroxo metal complexes.[1,3,8]
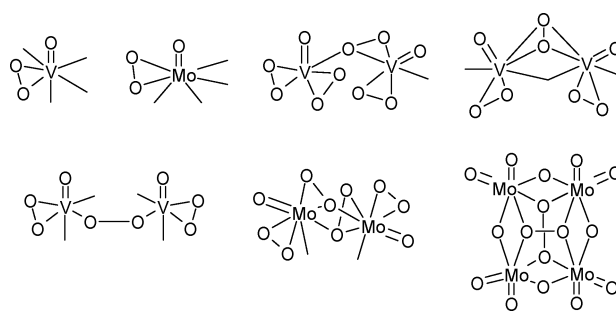
As far as the structure of the active complexes (indicated in Scheme 1) is concerned, an η^2 triangular arrangement of the bidentate peroxo group with the metal is very frequently observed.[1,2,3]

The classification of the peroxo structures was developed more than three decades ago by Vaska.[9] Interestingly, all of these have been found for different metals: in Scheme 2 selected examples, representative for the diverse coordination modes, are shown.[8,10]

Furthermore, binding to the metal of two or more peroxidic moieties is possible, with group 6 metals up to four peroxo groups have been observed.[11] V(v) poly-peroxo complexes have been characterized both in solution and in the solid state[12–14] and for some of these the oxidative chemistry has been elucidated.[15]

Bimetallic as well as tetranuclear μ-peroxo derivatives, with an $O_2{}^{2-}$ ligand bridging the metals in a variety of coordination modes, have been described.[1]

During the years, a number of books, chapters and reviews have been offered to researchers, bringing together the major structural and oxidative features of metal peroxides.[1–3,8,16–19]

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† Albeit being aware of the recent IUPAC suggestions to use peroxido to indicate the presence of the $O_2{}^{2-}$ group, throughout the paper we use the peroxo nomenclature in consideration of its large diffusion even in the most recent literature.

Scheme 2 Examples of the coordination modes for peroxo and μ-peroxo complexes.

In this review we concentrate on the recent achievements obtained in this field, while for less up-to-date literature interested readers are referred to relevant books.[1,20] With respect to the structural features of isolated peroxo species, an accurate collection of data has been published recently by Sergienko, both for vanadium[21] and molybdenum.[22]

The present review will not deal with the bio-related aspects of the chemistry of peroxo species, or with the rich literature related to polyoxometallates species, which in several cases, in catalytic processes, are the precursors of peroxidic active oxidants.

**Synthesis and structural aspects**

Peroxo complexes of the d^0 metals are typically prepared by reacting an aqueous solution of hydrogen peroxide with a metal precursor. The peroxidic species thus formed in solution can be isolated upon the addition of appropriate ligands. This quite old[23,24] but simple procedure is indeed general and is still applied with different metals and ligands. Almost all of the peroxo species collected in the following, Schemes 3 and 9 and in Tables 1, 2 and 3, have been prepared in such a mode. The order of addition of the peroxide and the ligand may vary and sometimes a ligand containing an oxo species is initially prepared and subsequently reacted with H_2O_2. For the vanadium derivatives, the most often used precursors are NH_4VO_3 or V_2O_5. In some instances, derivatives with vanadium in a lower oxidation state, such as vanadyl sulfate, are also utilized.

In the case of the molybdenum derivatives, which are likely the most numerous and best characterized species,[8] a very similar procedure applies. Typically, with Mo(vi), the formation of diperoxides is highly favoured, in fact the number of isolated and characterized monoperoxo complexes is lower in comparison with the diperoxo counterpart (see also the complexes reported in Table 3). Very often, peroxo molybdenum species are prepared by directly reacting MoO_3, or ammonium heptamolybdate, with an appropriate amount of hydrogen peroxide and the desired ligand, with the order of addition being somewhat flexible. Alternatively, the synthesis of the ligand containing a dioxo Mo precursor, followed by its reaction with H_2O_2 is a viable procedure that is often used.
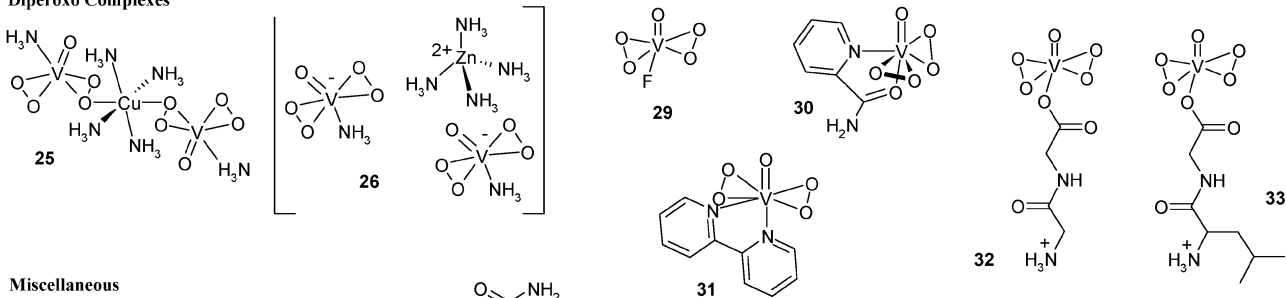
Interestingly, a peculiar synthesis has been done for monoperoxo V and Mo derivatives **12** and **59**. In the latter example, the Mo(iv) precursor was treated with dioxygen (Scheme 4). Such a procedure, which is rarely employed, was known for $[(CN)_4MoO(O_2)][(PPh_4)_2]$ and for some tetraphenyl and octaethyl substituted Mo porphyrins.[25]
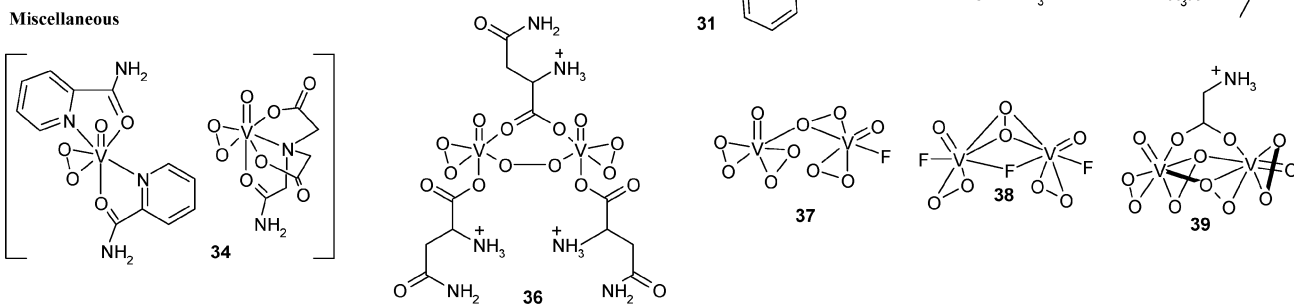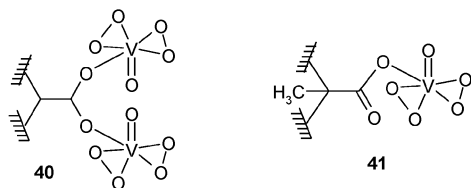
Monoperoxo complexes
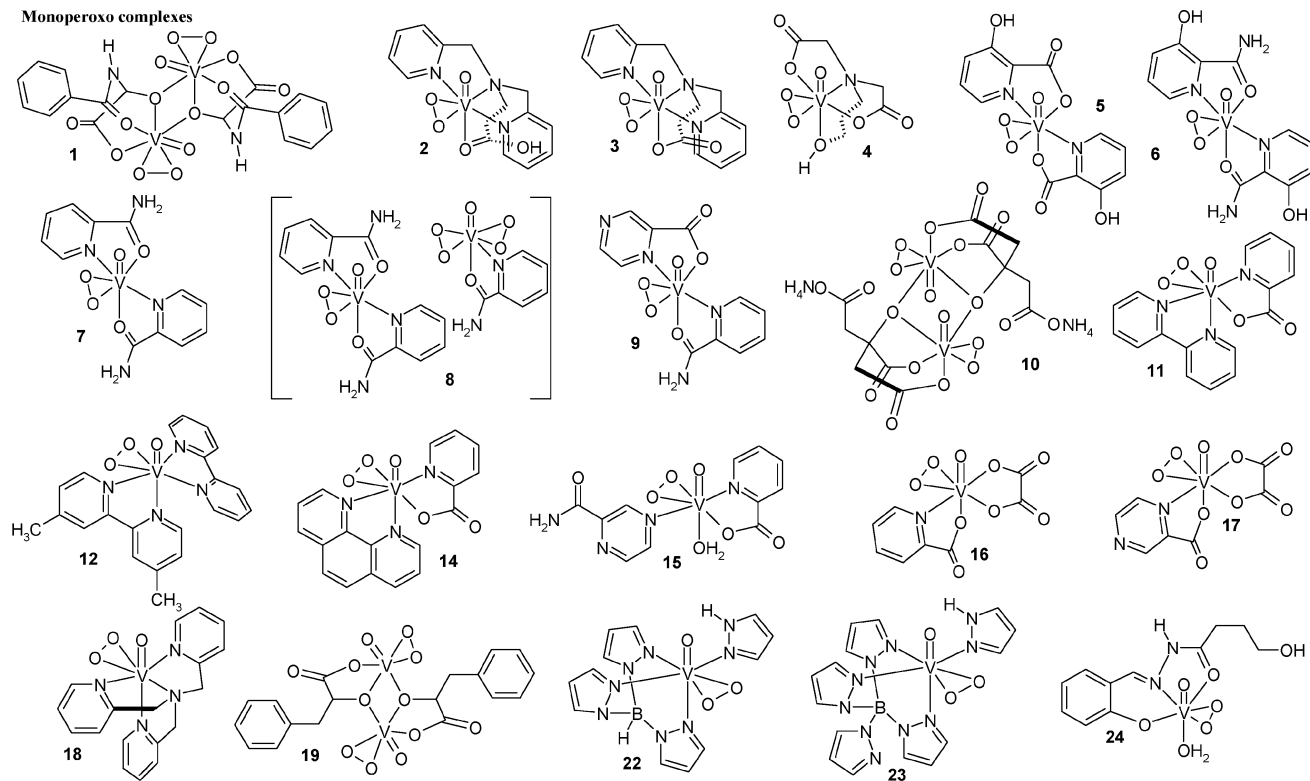
Diperoxo Complexes

Miscellaneous

Anchored

Scheme 3 The structure of isolated vanadium(v) peroxo complexes, numbered as in Tables 1 and 2. The charges on the complexes are omitted for clarity.

Table 1 Selected physicochemical properties of vanadium peroxo complexes

N.	Complex	Bond Lengths/Å			IR/cm⁻¹[a]					Ref.
		V=O	V(O₂)	O–O	V=O	(VO₂)ₛ		(VO₂)ₐₛ	O–O	
	Mono peroxo									
1a	(Bu₄N)₂[V₂O₂(O₂)₂(R-α-hhip)(S-α-hhip)]·5H₂O[b]	1.596	1.878, 1.894	1.441	972	590		562	928	29
1b	K₂[V₂O₂(O₂)₂(R-α-hhip)(S-α-hhip)]·5.5H₂O				968	572		553	920	29
1c	(H₄N)₂[V₂O₂(O₂)₂(R-α-hhip)(S-α-hhip)]·3H₂O				977		572			
1d	(Et₄N)₂[V₂O₂(O₂)₂(R-α-hhip)(S-α-hhip)]·8H₂O				973	595		573	918	29
2	[VO(O₂)Hbpa](ClO₄)[c]	1.588	1.878 (av)[d]	1.422	952		561		939	30
3	[VO(O₂)Hbpa]	1.597	1.868 (av)[d]	1.431						30
4	K[VO(O₂)heida][e]	1.599	1.878 (av)[d]	1.441	975	587		567	936	30
5a	NH₄[VO(O₂)(3-OH-pic)₂][f]	1.594	1.888 (av)[d]	1.426						30
5b	BuN₄[VO(O₂)(3-OH-pic)₂][g]	1.543	1.861 (av)[d]	1.352	957		575		945	30
6a	[VO(O₂)(3-OH-pa)₂](ClO₄)[h]				965			578	944	30
7	[VO(O₂)(pa)₂] (ClO₄)·3H₂O[i]	1.577, 1.566[j]	1.863, 1.913 1.890, 1.922	1.407 1.447	965		573		947	31
8	[VO(O₂)(pa)₂][VO(O₂)(pa)]·2H₂O				962		570		943, 920	31
9	[VO(O₂)(pca)]·H₂O[i,k]	1.604	1.869, 1.892	1.429	964		586		942	31
10a	(NH₄)₆[V₂O₂(O₂)₂(cit)₂]·4.5H₂O[l]	1.597	1.894, 1.895	1.430	965–952				930	32
10b	K₁₀[V₂O₂(O₂)₂(cit)₂][V₂O₂(O₂)₂(cit)₂]·20H₂O[l]	1.603	1.884, 1.889							33
10c	(NH₄)₆[V₂O₂(O₂)₂(cit)₂]₂·6H₂O[l]	1.595	1.878, 1.885							34
11	[VO(O₂)(pca)(bpy)][k,m]	1.605	1.862, 1.884	1.412	952	579		546	937	35
12	(BF₄)[VO(O₂)(Me₂bpy)₂][m]	1.556	1.869, 1.877	1.402	946				923	26
13a	(BF₄)[VO(O₂)(t-Bu₂bpy)₂][m]				963				927	26
13b	(BF₄)[V¹⁸O(¹⁸O₂)(t-Bu₂bpy)₂][m]				919				874	26
14	[VO(O₂)(pca)(phen)][k,n]	1.600	1.863, 1.889	1.438	962	582		549	933	35
15	[VO(O₂)(pca)(pcaa)(H₂O)]·H₂O[k,o]	1.598	1.871, 1.875	1.441	974	595		567	937	35
16	[NH₃(CH₂)₂NH₃][VO(O₂)(ox)(pic)]·2H₂O[p,q]	1.597	1.872, 1.932	1.439	962	571		545	927	36
17	[NH₃(CH₂)₂NH₃][VO(O₂)(ox)(pca)][k,p]	1.606	1.865, 1.920	1.430	956	580		547	927	36
18	[VO(O₂)(tpa)]Cl[r]	1.609	1.659, 1.863	1.434						37
19a	K₂[V₂O₂(O₂)₂(rac-3-phlact)₂][s]				980		562		923	38
19b	(Me₄N)₂[V₂O₂(O₂)₂(rac-3-phlact)₂][s]				982	576		541	933, 954	38
19c	(Bu₄N)₂[V₂O₂(O₂)₂(rac-3-phlact)₂][s]				990, 980		581		931	38
19d	(Pr₄N)(NH₄)₃[V₂O₂(O₂)₂(rac-3-phlact)₂][s]				983		582		929	38
20a	K₂[V₂O₂(O₂)₂(S-3-phlact)₂][s]				979		562		924	38
20b	(NH₄)₂[V₂O₂(O₂)₂(S-3-phlact)₂][s]				977		545		927, 938	38
20c	(Me₄N)₂[V₂O₂(O₂)₂(S-3-phlact)₂][s]				983	579		540	932, 954	38
20d	(Et₄N)₂[V₂O₂(O₂)₂(S-3-phlact)₂][s]				989	582		540	933	38
20e	(Pr₄N)₂[V₂O₂(O₂)₂(S-3-phlact)₂][s]				988	580		540	934	38
20f	(Bu₄N)₂[V₂O₂(O₂)₂(S-3-phlact)₂][s]				990	583		539	931	38
21a	(NH₄)₄[V₂O₂(O₂)₂(R3̄-phlact)₂][V₂O₂(O₂)₂(S-3-phlact)₂]·2H₂O·2MeOH·2H₂O₂[s]				982		567		923	38i
21b	(NEt₄)(NH₄)₃[V₂O₂(O₂)₂(R3̄-phlact)₂][V₂O₂(O₂)₂(S-3-phlact)₂][s]	1.590, 1.583	1.863, 1.885 1.863, 1.880	1.428 1.433	982	575			929	38
22	VO(O₂)(pzH)(HB(pz)₃)[t]	1.590	1.867, 1.886	1.410	983	566		535	939	39
23	VO(O₂)(pzH)(B(pz)₄)[t]				959	570		538	943	39
24	VO(O₂)(HSalhyb)·H₂O[u]	1.578	1.876, 1.891	1.429	978		562		921	40
	Di peroxo									
25	[{VO(O₂)₂(NH₃)₂}{μ-Cu(NH₃)₄}]	1.623	1.879, 1.895 1.894, 1.895	1.483 1.476	946		640	613	874	41
26	[Zn(NH₃)₄][VO(O₂)₂(NH₃)]₂	1.600 1.599	1.870, 1.885 1.899, 1.908 1.870, 1.875 1.875, 1.895	1.473 1.478 1.457 1.472	990, 975	631		612	881	41
27	Na[VO(O₂)₂(asn)]·H₂O[v]				949	649		557	869	42
28	Na[VO(O₂)₂(gln)]·H₂O[w]				953	660		540	873	42
29	[NH₃CH₂CH₂NH₃][VO(O₂)₂F]	1.614	1.886, 1.911 1.874, 1.906	1.476 1.471	944, 976	613, 640		490, 528	868, 884	43
30	(NH₄)[VO(O₂)₂(pa)] H₂O[i]	1.580	1.850, 1.907 1.853, 1.887							44
31a	Li[VO(O₂)₂(bpy)] nH₂O[m]	1.616	1.882, 1.907	1.463						

Table 1 (Contd.)

N.	Complex	Bond Lengths/Å			IR/cm⁻¹[a]					Ref.
		V=O	V(O₂)	O–O	V=O	(VO₂)s		(VO₂)as	O–O	
	Mono peroxo									
			1.882, 1.907	1.463						45
31b	Na[VO(O₂)₂(bpy)] nH₂O[m]	1.611	1.882, 1.915	1.460						
			1.885, 1.916	1.459						45
31c	K[VO(O₂)₂(bpy)] nH₂O[m]	1.624	1.891, 1.905	1.471						
			1.891, 1.915	1.471						45
31d	Rb[VO(O₂)₂(bpy)] nH₂O[m]	1.606	1.870, 1.890	1.458						
			1.874, 1.894	1.459						45
31e	Cs[VO(O₂)₂(bpy)] H₂O₂[m]	1.62	1.89, 1.9	1.5						
			1.84, 1.89	1.5						45
32a	Na[VO(O₂)₂(gly.gly)(H₂O)]·H₂O[x]				966	539		632	871	46
32b	K[VO(O₂)₂(gly.gly)(H₂O)]·H₂O[x]				968	542		630	870	46
33a	Na[VO(O₂)₂(gly.leu)(H₂O)]·H₂O[x,y]				967	540		634	873	46
33b	K[VO(O₂)₂(gly.leu)(H₂O)]·H₂O[x,y]				969	536		633	875	46
	Miscellaneous									
34	[VO(O₂)(pa)₂] [VO(O₂)(ada)·2H₂O[i,z]				969		578 (cat) 537 (an)		947 (cat) 865, 884 (an)	31
35	[V₂O₂(O₂)₃(asn)₃]·H₂O				954	631		562	859, 803	42
36	[V₂O₂(O₂)₃(gln)₃]·H₂O[w]				955	640		562	870, 809	42
37	Cs₃[V₂O₂(O₂)₄F]·H₂O	1.611, 1.603	1.876, 1.891 1.883, 1.879 1.944, 1.902 1.888, 1.871	1.470, 1.465, 1.467, 1.475	964	487		504	883(term) 869 (brid)	47
38	Cs₃[V₂O₂(O₂)₃F₃]·H₂O	1.603	1.857, 1.887 1.975, 2.055	1.455, 1.461	965	482		614	910	47
39a	(H₃O)₂[V₂(O)₂(μ₂:η²:η¹-O₂)₂(η²-O₂)₂(gly)]·H₂O	1.609	1.877, 1.906		947				878	48
		1.617	1.877, 1.926 1.871, 1.893 1.884, 1.937							
39b	K₂[V₂(O)₂(μ₂:η²:η¹-O₂)₂(η²-O₂)₂(gly)]·H₂O	2.056[aa]	1.894, 1.938		968				878	48
		2.047[aa]	1.865, 1.891 1.885, 1.929 1.869, 1.911							
	Anchored									
40	Na₃[V₂O₂(O₂)₄(carboxylate)]-PA[bb]				969	525		618	872	49
41	Na₃[V₂O₂(O₂)₄(carboxylate)]-PMA[cb]				966	526		637	875	49

[a] Assignment of the symmetric and asymmetric metal-peroxo stretch, when not clearly stated by the authors, was made on the basis of reported discussion[18] [b] α-hhip = α-hydroxyhippuric acid. [c] Hbpa = bis(picolyl)-β-alanine. [d] average. [e] H₂heida = N-(2-hydroxyethyl)iminodiacetic acid, [f] 3OH-pic = 3-hydroxypicolinic acid. [g] the similar neutral complex with t-BuOOH, [VO(tBuO₂)(3-OH-pic)₂], was also prepared, but no X ray analysis nor IR data are reported. [h] 3-OH-pa = 3-hydroxypicolylamide. [i] pa = picolinamide. [j] two different molecular structures cause disorder in solid state structure. [k] Hpca = 2-pyrazinecarboxylic acid. [l] cit = citrate. [m] bpy = 2,2′-bipyridine. [n] phen = 1,10-phenanthroline. [o] pcaa = 2-pyrazinecarboxyamide. [p] H₂ox = oxalic acid. [q] Hpic = picolinic acid. [r] tpa = tris(2-pyridylmethyl)amine. [s] 3-phlactH₂ = 3-phenyllactic acid. [t] pzH = pyrazole, HB(pz)₃ = tris(1H-pyrazol-1-yl)boron hydride. [u] H₂Salhyb = Schiff base from salicylaldehyde and 4-hydroxybutanoic acid hydrazide. [v] asn = asparagine. [w] gln = glutamine. [x] gly = glycine. [y] leu = leucine. [z] ada = carbamoylmethyliminodiacetate. [aa] as suggested from a referee, this length can be better attributed to a V–O single bond bridging to the countercation. [bb] PA = poly(acrylate). [cc] PMA = poly(methacrylate).
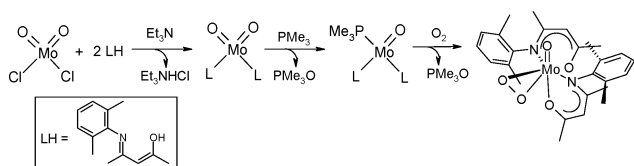
Scheme 4 The synthesis of the MoO(O₂)(ketim)₂ complex **59**.

Analogously, (BF₄)[VO(O₂)(Alk₂bpy)₂] complexes are prepared in excellent yields starting from the corresponding V^IV O(OH) precursors and dioxygen.[26] The intermediate formation of V-dioxo compounds has been demonstrated by using ¹H-NMR and UV-vis spectra.

Peroxo vanadium complexes

The variety of ligands used for preparing vanadium peroxo derivatives is shown in previous publications[1–3,13,18,21,22,27] and the most recent structures are collected in Scheme 3, while their salient structural and spectroscopic features are collated in Tables 1 and 2.

As to the solid state structure of vanadium peroxo compounds, the peroxide moieties can be considered in two different fashions: as an η² ligand, which occupies one coordination site, or as a chelating bidentate ligand. Without entering too much into the various geometric variants possible with both approaches, the interested readers are referred to the long discussion presented

Table 2 ^{51}V NMR chemical shifts of vanadium peroxo complexes

N.	Compound	^{51}V NMR/ppm	Solvent	Ref.
	Mono peroxo			
42	VO(O$_2$)$^+$	−595	H$_2$O pH $\cong$ 7.5	50
43	VO(O$_2$)(tf)$^{+a}$	−594	H$_2$O pH $\cong$ 7.5	50
44	VO(O$_2$)(pp)$^{+b}$	−605	H$_2$O pH $\cong$ 7.5	50
45	VO(O$_2$)(V-BrPO)$^{+c}$	−1155	H$_2$O pH $\cong$ 7.5	50
1	[V$_2$O$_2$(O$_2$)$_2$(R-α-hhip)(S-α-hhip)]$^{2−d}$	−576	H$_2$O	29
2	[VO(O$_2$)Hbpa](ClO$_4$)^e	−624 −610	H$_2$O/D$_2$O D$_2$O/EtOH	30
46	[VO(O$_2$)(bpg)]^f	−596 −583	H$_2$O/D$_2$O D$_2$O/EtOH	30
4	K[VO(O$_2$)heida]^g	−569	H$_2$O	30
5b	BuN$_4$[VO(O$_2$)(3-OH-pic)$_2$]^h	−597 (−575, −626)^i	H$_2$O	30
5c	K[VO(O$_2$)(3-OH-pic)$_2$]^h	−575 (−597, −626)^i	H$_2$O	30
47	[VO(tBuO$_2$)(3-OH-pic)$_2$]^h	−591, −620^j	H$_2$O	30
48	[VO(tBuO$_2$)(3-OH-pa)$_2$]$^{2+k}$	−589	H$_2$O	30
6a	[VO(O$_2$)(3-OH-pa)$_2$](ClO$_4$)^k	−590 −613^l	H$_2$O	30
6b	[VO(O$_2$)(3-OH-pa)$_2$]Cl^k	−590 −611^m	H$_2$O	30
7	[VO(O$_2$)(pa)$_2$]$^{+n}$	−603	H$_2$O, pH 0–3.6	31
11	[VO(O$_2$)(pca)(bpy)]^{o,p}	−560	CH$_2$Cl$_2$	35
14	[VO(O$_2$)(pca)(phen)]^{o,q}	−562	CH$_2$Cl$_2$	35
15	[VO(O$_2$)(pca)(pcaa)(H$_2$O)]·H$_2$O^{o,r}	br, −520 to −545	H$_2$O, pH 3.75	35
16	[VO(O$_2$)(ox)(pic)]$^{2−s,t}$	−604	H$_2$O	36
17	[VO(O$_2$)(ox)(pca)]$^{2−o,t}$	−629	H$_2$O	36
18	[V$_2$O$_2$(O$_2$)$_2$(rac-3-phlact)$_2$]$^{2−u}$	−604	H$_2$O	38
24	VO(O$_2$)(HSalhyb)·H$_2$O^v	−551	CD$_3$OD	40
22	VO(O$_2$)(pzH)(HB(pz)$_3$)^w	−623	CDCl$_3$	39
23	VO(O$_2$)(pzH)(B(pz)$_4$)^w	−625, −707	CDCl$_3$	39
49	[VO(O$_2$)(ma)$_2$]$^{−x}$	−563.6	H$_2$O(NaCl)	51, 52
50	[VO(O$_2$)(ur)]$^{2−y}$	−610	H$_2$O(NaCl)	51, 52
	Di peroxo			
51	[VO(O$_2$)$_2$ox]$^{3−t}$	−738	D$_2$O	53
52	[VO(O$_2$)$_2$(pp)]$^{−b}$	−700	H$_2$O	50
29	[VO(O$_2$)$_2$F]$^{2−}$	−714, d (J$_{VF}$ = 163 Hz), −689	H$_2$O	43, 47
53	[VO(O$_2$)$_2$(H$_2$O)]$^−$	−700	H$_2$O	43
54	[V$_2$O$_2$(O$_2$)$_4$(OH)]$^{3−}$	−760	H$_2$O	43
55	[VO(O$_2$)$_2$(pa)]$^{−n}$	−732	H$_2$O/D$_2$O	44
56	[VO(O$_2$)$_2$(Ma)]$^{2−x}$	−735	H$_2$O(NaCl)	51, 52
57	[VO(O$_2$)$_2$(Ur)]$^{2−y}$	−740	H$_2$O(NaCl)	51, 52
27	[VO(O$_2$)$_2$(asn)]$^{−z}$	−695	H$_2$O	42
28	[VO(O$_2$)$_2$(gln)]$^{−aa}$	−695	H$_2$O	42
58	[VO(O$_2$)$_2$(oxazole)]$^−$	−726	H$_2$O/D$_2$O	54
	miscellaneous			
35	V$_2$O$_2$(O$_2$)$_3$(asn)$_3$^{z}	−694	H$_2$O	42
36	V$_2$O$_2$(O$_2$)$_3$(gln)$_3$^{aa}	−694	H$_2$O	42

^{a} tf = bovine apo-transferrine. ^{b} pp = bovine prostatic acid phosphatase. ^{c} V-BrPO = vanadate dependent bromeperoxidase. ^{d} α-hhip = α-hydroxyhippuric acid. ^{e} Hbpa = bis(picolyl)-β-alanine. ^{f} bpg = bis(picolyl)glycinate. ^{g} H$_2$heida = N-(2-hydroxyethyl)iminodiacetic acid. ^{h} 3-OH-pic = 3-hydroxypicolinic acid. ^{i} the intensity ratio depends on pH; the first value indicates the dominant signal. ^{j} 22% and 35%, respectively, with 43% [VO(tBuO$_2$)(H$_2$O)$_x$]$^{2+}$, at −531 ppm. ^{k} 3-OH-pa = 3-hydroxy-picolylamide. ^{l} 3 : 2. ^{m} 44 : 56. ^{n} pa = picolinamide. ^{o} Hpca = 2-pyrazinecarboxylic acid. ^{p} bpy = 2,2′-bipyridine. ^{q} phen = 1,10-phenanthroline. ^{r} pcaa = 2-pyrazinecarboxyamide. ^{s} Hpic = picolinic acid. ^{t} H$_2$ox = oxalic acid. ^{u} 3-phlactH$_2$ = 3-phenyllactic acid. ^{v} H$_2$Salhyb = Schiff base from salicylaldehyde and 4-hydroxybutanoic acid hydrazide. ^{w} pzH = pyrazole, HB(pz)$_3$ = tris(1H-pyrazol-1-yl)boron hydride. ^{x} ma = maltol. ^{y} ur = uridine. ^{z} asn = asparagine. ^{aa} gln = glutamine.

by Sergienko.[21] Considering the peroxo ligand as a bidentate one, the most widespread structure is the pentagonal bipyramid found with monoperoxo, as well as for diperoxo derivatives. Very few cases of a sixfold pentagonal pyramid have been reported,[28] mainly for diperoxo complexes, for recent examples see **26**, **29**, **32**, **33**, **37** and **40**.

The structural features of the peroxovanadium species summarized in Table 1 are in agreement with those of previously synthesized complexes.[1,3,8,20,21] If the typical distortions observed in the coordination polyhedra for different vanadium species are considered,[21] the features can be summarised as in Fig. 1: geometric parameters are very similar, IR frequencies are comparable as well and the oxo and peroxo groups are in *cis* position.

This is true also with more complicated, often polynuclear, structures: see, as just a few examples, complexes **10**, **39** and related structures.[32–34,48,55]

A review with a collection of salient UV-vis data for monoperoxo vanadium species recently appeared.[27]

Quite different is the scenario of the ^{51}V-NMR chemical shifts, related data are collected in Table 2. It is evident that the range where monoperoxo species resonate (from −630 to −510 ppm from VOCl$_3$) is quite far away from that of diperoxo vanadates (from −740 to −690 ppm). Such a difference has been often used to study the formation equilibria of the various peroxo derivatives, as a function of the excesses of H$_2$O$_2$. It is to be recalled here that, when vanadates are dissolved in aqueous solutions, in the presence

Table 3 Selected physicochemical properties of molybdenum peroxo complexes

N.	Complex	Bond lengths/Å			IR/cm-1				Ref.
		Mo=O	Mo(O₂)	O–O	Mo=O	(MoO₂)ₛ	(MoO₂)ₐₛ	O–O	
	Monoperoxo								
59	MoO(O₂)(ketim)₂[a]	1.673	1.936, 1.951	—	—				66
60	MoO(O₂)Cl₂(OPMePh₂)₂	1.705	1.839, 1.904	1.316	956	597	550	920	67, 68
61	MoO(O₂)Cl₂(dppmO₂)[b]				965			920	68
62	(NH₄)₂[Mo₂O₂(O₂)₂(μ-OH)₂(ox)₂][c]	1.688	1.962, 1.976	1.458	920	ca.650	ca.600	874	69
63	MoO₂(QO)₂[d]				960			915	70
64	Mo₄O₆(O₂)₂(μ₃-O)₂{(μ₂-O, μ₃-OC₈H₁₄}₂(OPMePh₂)₂[e]	1.659	1.894, 1.910	1.395	953	664	649	889	71
65	MoO(O₂)Cl₂(dmso)₂[f]	1.675	1.856, 1.913	1.324	[p]	[p]	[p]	1138	72
66	CpMoO(O₂)CH₃[g]				951		565	877	73
	Diperoxo								
67a	[Ph₃P(CH₂)₃PPh₃][MoO(O₂)₂ox]·H₂O[c]				937	690	580	855	74
67b	(NH₄)₂[MoO(O₂)₂(ox)][c]	1.671	1.919, 1.955	1.475	967	ca.650	ca.600	865	69
68a	(NH₄)₂[MoO(O₂)₂(H₂cit)][h]				954	ca.650	ca.600	856	69
68b	K₄[MoO(O₂)₂cit]·4H₂O[h]	1.688	1.933, 1.985		946	650	577	853	75
68c	K₄[MoO(O₂)₂(Hcit)H(Hcit)(O₂)₂OMo]6H₂O[h]	1.684	1.926, 1.975 / 1.930, 1.980		942	647	582	857	75
69	(NH₄)₂[MoO(O₂)₂(H₂tart)]·2H₂O[i]				950	ca.650	ca.600	848	69
70	(NH₄)₂[MoO(O₂)₂(H₂glyc)]·0.5 EtOH[j]	1.680	1.941, 1.986 / 1.952, 1.973	1.484	956, 930	ca.650	ca.600	849	69
71a	(NH₄)₂[MoO(O₂)₂(Hmal)]·H₂O[k]				948	ca.650	ca.600	856	69
71b	K₂ₙ[MoO(O₂)₂(S-Hmal)]ₙ·nH₂O[k]	1.693	1.942, 1.972 / 1.942, 1.967		947	639	576	859	75
72	MoO(O₂)₂(OPMePh₂)₂	1.665 / 1.918, 1.959	1.919, 1.951 / 1.471	1.473	951	657	582	865	76
73	Mo(O)(O₂)₂(dppmO₂)[b]	1.63	1.813, 1.894 / 1.802, 1.962	1.404 / 1.420	961, 953			864, 875	68
74	MoO(O₂)₂(H₂O)(OPMePh₂)	1.671	1.909, 1.934 / 1.909, 1.938	1.450 / 1.461	951	716	693	891	71
75	PPh₄[MoO(O₂)₂(QO)][d]	1.684	1.910, 1.948 / 1.909, 1.953		945	720	645	810, 845	70
76	[MoO(O₂)₂4,4′-bipy]ₙ[l]				927	620	558	843	77
77	[PPh₄]₂[(Me)₂SiO₂{Mo₂O₂(μ-O₂)₂(O₂)₂}]	1.681	1.924, 1.934 / 1.903, 1.986	1.466, 1.474 / 1.483, 1.479	971, 958	585	528	868	78
78	[PPh₄]₂[(i-Bu)₂SiO₂{Mo₂O₂(μ-O₂)₂(O₂)₂}]	1.680	1.925, 1.930 / 1.917, 1.995	1.479, 1.467, / 1.475, 1.470	963, 948	584	526	866	78
79	[PPh₄]₂[(Me)(CH₂Cl)SiO₂{Mo₂O₂(μ-O₂)₂(O₂)₂}]	1.682	1.926, 1.926 / 1.909, 1.996	1.469, 1.464, / 1.479, 1.474	966	585	525	866	78
80	K₈[Mo₄O₁₂(O₂)₂]	1.716, 1.728	*1.908, 1.912* / *2.200, 2.277*	1.467	835, 889			928, 951	79
81a	K₂[Mo₂O₂(μ-O)(O₂)₂(H₂O)₂]·2 H₂O	1.688 / 1.911μ	1.943, 1.957 / 1.945, 1.967	1.477, 1.483, / 1.479, 1.482	961	578	531	855	80
81b	(2-MepyH,NH₄)[Mo₂O₂(μ-O)(O₂)₂(H₂O)₂]·2H₂O[m]	1.677 / 1.953μ	1.949, 1.975 / 1.938, 1.962	1.483, 1.484, / 1.482, 1.485	973	570	541	851,868	80
81c	(2-MepyH,Na)[Mo₂O₂(μ-O)(O₂)₂(H₂O)₂]·2H₂O[m]	1.680 / 1.934μ	1.957, 1.986 / 1.933, 1.953	1.474, 1.485, / 1.474, 1.481	922	593	559	891	80
82	[MoO(O₂)₂(4-MepyO)₂]·H₂O[n]	1.6885	1.9314, 1.9411 / 1.9314, 1.9522	1.4735, 1.4795					81
83a	[MoO(O₂)₂(MBB)][o]				933	602	775	865	82
83b	[MoO(O₂)₂(PBB)][o]				952	598	758	840	82
83c	[MoO(O₂)₂(MBU)][o]				926	606	760	847	82
83d	[MoO(O₂)₂(PBU)][o]				951	595	760	839	82
83e	[MoO(O₂)₂(MBTU)][o]				926	607	770	839	82
83f	[MoO(O₂)₂(PBTU)][o]				935	618	707	810	82
	Tetraperoxo								
84a	Li₂[Mo(O₂)₄]·4H₂O	—	1.989, 1.955 / 1.971, 1.951 / 1.933, 1.931 / 1.977, 1.958	1.482 / 1.486 / 1.477 / 1.484	—	607	567	842	83

Table 3 (*Contd.*)

N.	Complex	Bond lengths/Å			IR/cm-1				Ref.
		Mo=O	Mo(O$_2$)	O–O	Mo=O	(MoO$_2$)$_s$	(MoO$_2$)$_{as}$	O–O	
	Monoperoxo								
84b	Na$_2$[Mo(O$_2$)$_4$]·4H$_2$O	—	1.970, 1.979	1.483	—	582	557	836	84
			1.939, 1.960	1.487					
			1.974, 1.953	1.481					
			1.931, 1.940	1.484					
84c	Rb$_2$[Mo(O$_2$)$_4$]				—	607	551	858	84
84d	Cs$_2$[Mo(O$_2$)$_4$]				—	606	557	843	84

[a] ketim = 4-(2,6-dimethylphenylimino)pent-2-en-1-olate. [b] dppmO$_2$ = diphenylphosphinomethane oxide. [c] H$_2$ox = oxalic acid, ox = oxalate C$_2$O$_4$$^{2-}$. [d] QO = 8-quinolinolate. [e] C$_8$H$_{14}$ = cyclooctene. [f] dmso = dimethylsulfoxide. [g] Cp = η^5-cyclopentadienyl. [h] H$_4$cit = citric acid. [i] H$_2$tart = tartaric acid. [j] Hglyc = glycolic acid. [k] H$_2$mal = malic acid. [l] 4,4′-bipy = 4,4′-bipyridyl. [m] 2-Mepy = 2-methylpyridine. [n] 4-Mepy = 4-methylpyridine. [o] Mannich base, see Scheme 9. [p] IR data of peroxo complexes likely refer to the parent dioxo precursor reported in the same paper.
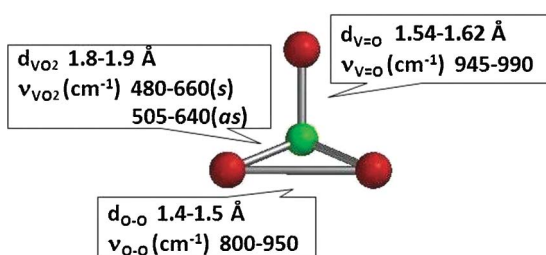

Fig. 1 Physicochemical features of V(v) peroxo complexes.

of hydrogen peroxide, several species can be formed depending on the pH, the ionic strength and the ratio of H$_2$O$_2$: V. All of them are in equilibrium and the prevalence of the different types of peroxidic complexes is strongly influenced by pH. Higher values favour species with more peroxo groups bound to the metal.
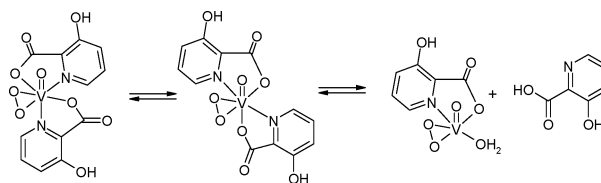
Several research groups studied such equilibria, particularly to shed light on the nature of the real oxidant in the catalytic systems.[1,3] More recently, an interesting work appeared, where experimental and computed ^{51}V-NMR chemical shifts were used to assess the solution structures.[56] In such a way, two high field resonances have been attributed to tetra- ($\delta < -730$ ppm for [V(O$_2$)$_4$]$^{3-}$) and tri-peroxovanadates ($\delta < -830$ ppm for [VO(O$_2$)$_2$OOH]$^{2-}$), complexes rarely observed.

A particular example of ^{51}V-NMR analysis of monoperoxo species, in water in the presence of proteins as ligands, has been described by Rehder[50] who showed that mono peroxovanadate bound to bovine apo-transferrine (tf) or to bovine prostatic acid phosphatase (pp) has an almost unbiased chemical shift ($\delta \cong -600$ ppm) (see Table 2, compounds **43**, **44** and **45**), while in the presence of vanadium dependent bromo peroxidase (V-BrPO) such a signal is extremely shielded ($\delta \cong -1155$ ppm). The high shielding of vanadate in the presence of a peptide ligand has been predicted with DFT calculations.[57]

In the same year, Rehder[30] published the structure of some oxo monoperoxo vanadium species (complexes **2–6** in Table 1), in such a paper a detailed description of the influence of the nature of the ligands and of the experimental conditions on the ^{51}V-NMR chemical shifts is reported.

To note (see Table 2), that in the presence of ligands such as 3-hydroxypicolinic acid, biligated complexes may undergo a slow equilibrium between two species containing the pyridine
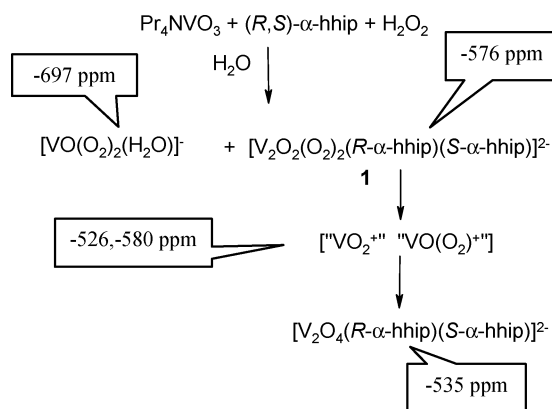
nitrogen *cis* or *trans* with respect to the peroxo group, as observed in complexes **5** and **47**, thus showing two different ^{51}V-NMR resonances (see Scheme 5).[30]
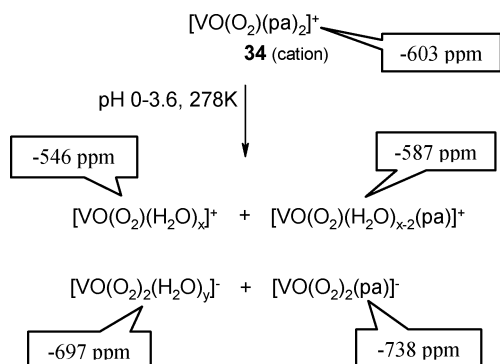

Scheme 5 The exchange equilibria for complex **5**.

The use of ^{17}O-NMR, a technique rarely used for peroxo species, considering the difficulties to obtain labelled H$_2$^{17}O$_2$, is also presented. Notably, the inequivalence of the ^{17}O-NMR peroxidic signals for the vanadium diperoxo anion was observed.[30]

Complex **1**, a dimeric diperoxo species with racemic α-hydroxyhippuric acid as the ligand, exhibits in solution a decomposition pattern to its reduced forms, which can be followed with ^{51}V-NMR, as indicated in Scheme 6.[29] A distinctive behaviour is the formation in solution of a mixed dioxo and oxo-peroxo vanadium(v) dimeric species, which shows two resonances at $\delta = -526$ and -580 ppm.

Scheme 6 The decomposition pattern, in aqueous solutions, for complex **1** prepared *in situ*.
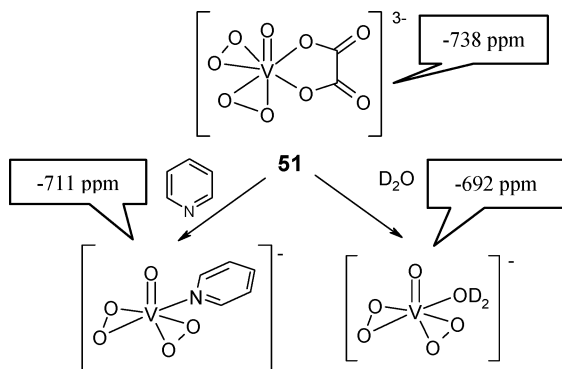
Another representative example of the speciation analysis of peroxo vanadates in an acid aqueous solution has been reported

with complex **34** (see Scheme 7, where only the cationic moiety is indicated). To note, the presence of a basic ligand generates a remarkable difference in the chemical shifts, both on the mono and di-peroxo vanadates,[31] an effect well known in the literature.[58,59]

Scheme 7 The equilibria for the cationic moiety of complex **34** in acid water solutions.

In Scheme 8, a similar equilibrium in aqueous solution is shown for the diperoxo vanadium complex **51**.[53] The dependence of the vanadium peroxides resonances on the pH of the solution and the temperature is clearly shown. The peak at −711 ppm moves toward lower fields with an increase either of the temperature or of the pH of the solution. The attribution of the peaks has been supported by 2D ^{1}H-DOSY experiments, measuring the diffusion rates of the different complexes.

Scheme 8 The exchange equilibria for complex **51**, in the presence of pyridine, as measured with ^{51}V-NMR experiments.

A similar work, with oxazole as the ligand, appeared more recently,[54] where the experimental data were also supported with theoretical calculations. A pentagonal pyramidal arrangement for [VO(O$_2$)$_2$(oxazole)]$^-$ is proposed.

Other speciation studies in aqueous solution for peroxo and diperoxo vanadates, in the presence of different types of bio-related ligands, have been reported.[51,52] Those kinds of investigations were stimulated by the finding of the insulin-enhancing effects exhibited by vanadate and peroxovanadate complexes.[60,61]

Studies with aminoacids or small peptides are, on the other hand, more related to the inhibition of phosphoprotein hydrolysis by the peroxovanadium derivatives,[46] as well as with the modelling of vanadium dependent haloperoxidases.[61]

Also, fluorine containing diperoxovanadate exhibits its ^{51}V-NMR resonance in the typical range ($\delta = -711$ ppm with a J_{VF}

$\cong$ 163 Hz).[43] When the more complex bimetallic species **37** and **38** are dissolved in water, [VO(O$_2$)$_2$(H$_2$O)]$^-$ and [VO(O$_2$)$_2$F]$^{2-}$ have been detected as the most important species.[47]

The formation of fluoro diperoxo vanadium anion, from vanadate and hydrogen peroxide, has been observed in a water–hydrophilic ionic liquid (bmimBF$_4$) mixture.[62]

Remaining in the field of speciation in aqueous peroxovanadate-ligands systems, some bio-related works have been published by Salifoglou and colleagues[32–34,48,55,63] The papers refer to the quite complex equilibria that are taking place in water at physiological conditions, between vanadium and biogenic ligands such as citrate or glycine. Interestingly, polynuclear peroxo complexes are formed with both ligands, species **10** and **39** in Table 1.

ESI-MS studies for the amino acid containing vanadium peroxo species have been reported[64] and compared with previous ones.[19,65]

Peroxo molybdenum complexes

Also in the case of molybdenum peroxo derivatives, several different types of ligands have been used. Scheme 9 collects the compounds whose solid state structures have been published in recent years. The relevant structural and spectroscopic features are shown in Fig. 2 and in Table 3.
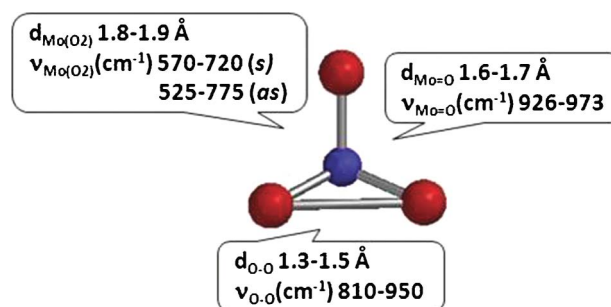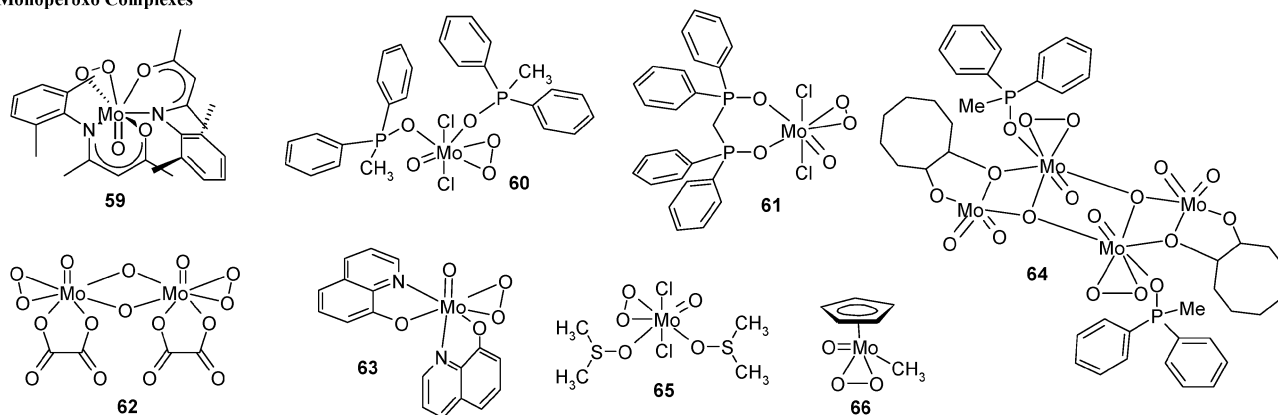

Fig. 2 The physicochemical features of Mo(VI) peroxo complexes.

A typical behaviour of the molybdenum based peroxides is the lower stability of the monoperoxo derivatives as compared with their diperoxo counterparts. This fact is well accounted for by the smaller number of isolated monoperoxo species collected in Scheme 9 and Table 3. Such a feature has been underlined also in the past.[1,2,3]
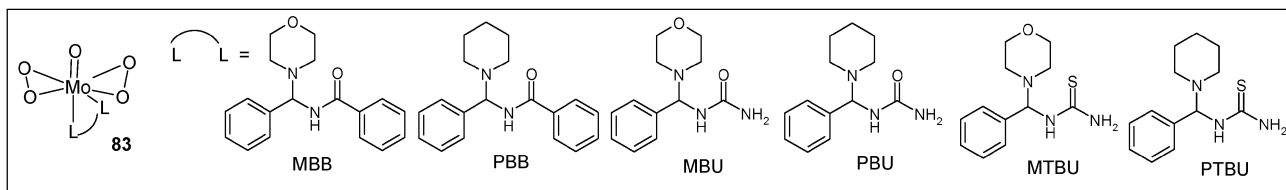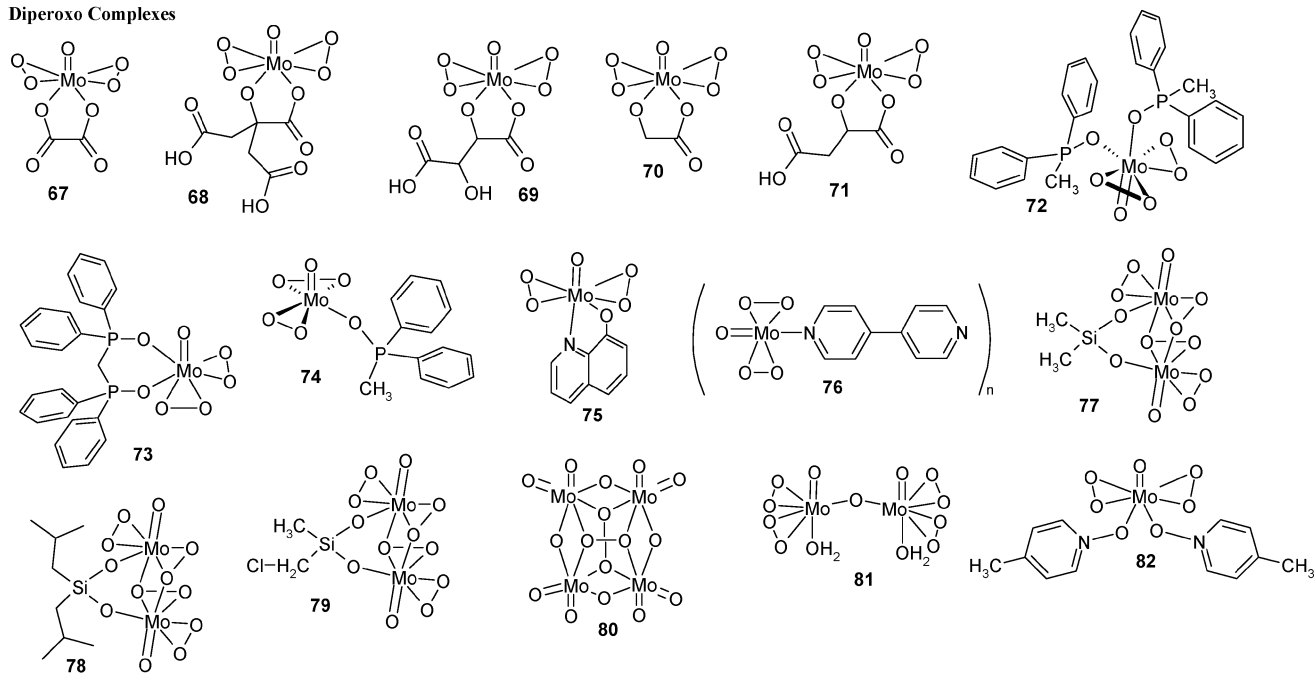
From the inspection of the solid state structures, it is visible that the derivatives collected here display the same motifs already known: a pentagonal bipyramidal structure, with the oxo oxygen at one apex and the η^2 peroxo moiety(ies) in the equatorial plane *cis* to the oxo oxygen. The slight length difference between the two Mo–O bonds of the peroxide bridge is a general feature, the longer bond being closer to the site of coordination occupied by the ligand. Therefore, this "hindrance" may well be the reason for such asymmetry.

The IR frequencies related to the MoO(O$_2$) group are, as in the case of the parent vanadium species, in a quite narrow range. To note, the values of v_{O-O} = 810–950 cm^{-1} are very similar to those measured for the peroxidic oxygens bound to the vanadium atom. On the other hand, Mo metal–oxo and metal–peroxo bonds, respectively, exhibit lower and higher wavenumbers in comparison with vanadium derivatives (see Fig. 1 and 2).
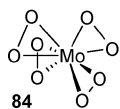
Monoperoxo Complexes

Diperoxo Complexes

Tetraperoxo Complexes

Scheme 9 The structure of isolated molybdenum(VI) peroxo complexes, numbered as in Table 3. The charges on the complexes are omitted for clarity.

These features remain nearly unchanged also for polynuclear or polyperoxo species.

Complex **80**, a peculiar tetra-molybdenum diperoxo derivative,[79] exhibits a double μ_4 arrangement of the two peroxidic moiety and four μ–oxo bridges with a shorter Mo–O bond. The IR frequencies

are, however, not very different from those observed in the other species reported in Table 3.

Oxo mono peroxo Mo species **60** and **65**, which contain chloride ligands,[67,72] display a short O–O bond length, $\cong 1.32$ Å, which is an intermediate value between that of H_2O_2 (1.44 Å) and that of O_2

(1.21 Å). This could be a characteristic sign for a Mo(v)superoxide species, however the absence of any EPR signal unquestionably points to Mo(vi)-peroxo as the correct electronic configuration.

Still, in the examples of monoperoxo derivatives, complex **66**, CpMoO(O$_2$)CH$_3$, is representative of the cyclopentadiene Mo(vi) species, which are prepared by oxidation of the Mo(ii) precursor,[73,85] through the formation of a dioxo Mo(vi) intermediate, with t-butylhydroperoxide (TBHP).

As already discussed in the previous paragraph for vanadium compounds, it cannot be anticipated that the structure in solution is identical or even similar to the solid state one. To obtain information concerning the solution structure, the one actually involved in reactivity, the use of heteronuclear NMR is a key tool. However, in the case of peroxomolybdate, albeit application of ^{95}Mo or ^{97}Mo NMR spectroscopy is possible,[86] not many studies have been published. In some instances the analysis of the equilibria can be done by following the signals of the ligands. In particular, when phosphorous is present, ^{31}P-NMR technique can be applied conveniently.

Theoretical calculations

Theoretical calculations have been performed for several V and Mo peroxo species, in particular to obtain an indication on the stability of the different catalysts that can be formed upon coordination of peroxide to the metal centre, or to shed light on the mechanistic pathway of oxidation.

Worthy to note are reports that refer to the application of different types of theoretical analysis to highlight the reasons behind the chemoselectivity shown by peroxo molybdenum species.

When divanadium triperoxo complexes **35** and **36**[42] were analysed with DFT methods,[87] it was shown that the peroxo groups (bridged vs. side-on) are non equivalent. Furthermore, the electrophilicity of the bridged peroxo group is higher, thus rendering them as the preferential site of attack for bromide ions in oxidative bromination processes.

DFT calculations were also performed to discriminate between the different mechanistic proposals for olefin epoxidation, with H$_2$O$_2$ catalysed by salen or salan (ligands prepared from salicylaldehyde derivatives and diamines) vanadium complexes.[88–90] As in several previous instances, also with quite complex systems, evidence favouring the Sharpless mechanism has been obtained.

The same theoretical approach has been used to analyse the structure of the intermediates involved in the oxidations of hydrocarbons with H$_2$O$_2$, V(v) and carboxylic acids. The proposed formation of ozone in such processes appears to be substantiated by the calculations.[91,92]

The same authors have also used DFT calculations to model the interaction of water molecules with mono and di-peroxo vanadates.[93]

A similar approach has been used to identify a mechanistic pathway for the oxidation of nitrogen with peroxo vanadates. The fate of the N$_2$O formed appears to be dominated by its addition to the V=O bond to form hyponitrite.[94]
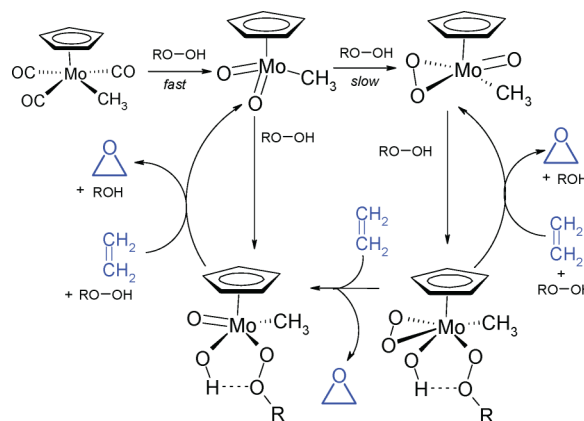
A few years before, Bühl used density functional studies to prove once again the principal steps in the oxidation of olefins with peroxo vanadium derivatives. In the same paper, he also used such studies, taking into account the effects of solvation and dynamics, to model the ^{51}V-NMR chemical shifts in aqueous

solutions. A good agreement with experimental data was obtained for the diperoxo complexes containing imidazole and pyridine ligands.[95]

In a paper authored by Shiga,[96] the paired interacting orbitals analysis (PIOs) showed that the olefin epoxidation reaction, modelled with ethylene, is influenced by the variation of overlap repulsion between the orbitals of the substrate and the occupied orbitals of the Mo peroxo complex. When increasingly hindered amines are coordinated to the metal centre, such repulsion rises, thus rendering the reaction less feasible. On the other hand, the energy of the MO orbitals of the alkoxy species, which forms before the hydrogen abstraction step, appears not to be influenced by the coordination of the amines.

DFT calculations at the B3LYP level were used to explain the chemoselectivity observed in the electrophilic oxidation of unsaturated sulfides to the corresponding sulfoxides (or even sulfones).[97] Such selectivity has been explained on the basis of the predominant orbital interactions observed in the calculated TS. It has been shown that the energy level of the sulfur lone pair (HOMO) is sufficiently high with respect to that of the π electrons (HOMO-1) of the double bond to account for the experimental data. Further calculation, refined with the addition of solvent effects (SCRF approach), allowed the prediction of a decrease of the chemoselectivity with increasing solvent polarity.

Very recently, the mechanism of catalysis for an η^5-cyclopentadienyl molybdenum species, used in the epoxidation of olefins with TBHP (complex **66**[73] see Scheme 10), was studied with DFT calculations at the B3LYP level.[98]

Scheme 10 The calculated reaction mechanism for olefin epoxidation with alkylhydroperoxides, catalysed by complex **66**.
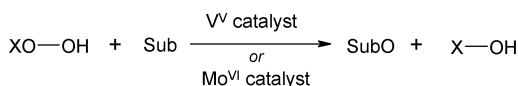
In this example the barriers obtained for several different pathways are very similar, therefore clear-cut evidence of which one is operating was not available. The theoretical data (Scheme 10) are in agreement with the mechanistic studies reported from the same research group.[73] The authors also indicate that the calculated solvent effect is negligible.

Reactivity

The enhancement of the reactivity of peroxides in the presence of metal catalysis is very well known, moreover, for several types of reactions the mechanistic details have been elucidated. To note, in

a number of cases, support for the mechanistic proposals has been obtained with theoretical calculations.

With very few notable exceptions,[1,3,8,17] Mo(VI) and V(V) peroxo species behave as electrophilic oxygen transfer reagents, thus reacting preferentially with the more nucleophilic functional group present in the molecule. In several instances the chemoselectivity observed is very high, when not exclusive. The simple and general equation that describes these reactions is shown in Scheme 11.

$$XO\!-\!OH + Sub \xrightarrow[Mo^{VI} \text{ catalyst}]{V^V \text{ catalyst} \atop or} SubO + X\!-\!OH$$

X = H, alkyl
Sub = phosphines, amines, sulfides, sulfoxides, alkenes, alcohols, etc.

Scheme 11 The oxidation reactions with peroxides catalysed by V(V) or Mo(VI) precursors.

From the mechanistic point of view, when a nucleophile reacts with an η^2-peroxometal complex, a direct attack on the substrate by the electrophilic oxygen is envisaged and no intermediates are present, but only a spirocyclic transition state is involved along the reaction coordinate (Sharpless mechanism)[1,3,8]

This mechanism has a close relationship with the one accepted for the oxidation reactions with peracids. A different mechanism was proposed in the past,[1,2,3,8] with the occurrence of a peroxometallacyclic intermediate. However, experimental and theoretical evidence points against such a route (see also the previous paragraph), with a few exceptions observed with specific substrates. Here, we will not recall in detail those quite old and meticulous studies, which have already been collected and described recently.[1,2]

As far as vanadium peroxides are concerned, there is also evidence of a quite complex radical oxidative reactivity toward alkanes and aromatics, which has been thoroughly examined by diverse research groups, also very recently.[99,100]
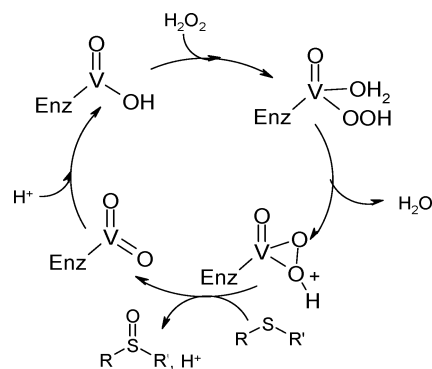
It may be, however, interesting to note that sometimes "old oxidation chemistry" is rediscovered, without taking entirely into consideration the recent achievements in the field. An example is the oxidation of chalcogenides with the known Mimoun complex[8,23] MoO(O$_2$)$_2$HMPA(H$_2$O).[101]

A peculiar aspect in the Mo(VI) catalysis appears when metal precursors are treated with a very high excess of hydrogen peroxide, particularly in basic media. In such conditions, a composite mixture of peroxo complexes forms, where mono, di and tetraperoxo derivatives are present in low amounts, while the triperoxo species is the predominant one. This latter compound is able, in the absence of other reactive substrates, to oxidize H$_2$O$_2$ to singlet oxygen.[102]

To note, an ample collection (up to the end of 2003) of the works appearing in the literature concerning the reactivity of vanadium and molybdenum peroxo derivatives toward several functional groups is present in the Patai book dedicated to the chemistry of peroxides.[1]

A hot research topic connected with the reactivity of vanadium peroxo derivatives refers to model systems for the oxidative ability of vanadium-dependent haloperoxidases enzymes, VHPOs. Such natural systems efficiently perform the oxidation of halides to hypohalous acids and of sulfides to the corresponding sulfoxides.

In particular, the accepted mechanism for such reactions can be sketched as indicated in Scheme 12.

Scheme 12 The simplified mechanism for VHPOs catalysed sulfoxidations.

Complex **4**, K[VO(O$_2$)heida],[30,103] is likely the best established functional model for VHPOs, such a complex has been used to propose a mechanistic pathway, where a key step is the protonation of a peroxo oxygen to form an hydroperoxo intermediate,[30] which reacts more easily with the nucleophilic substrate, *i.e.* halides or sulfides.

In order to locate the site of the protonation, investigations were performed with experimental spectroscopy[104] (XANES, X-ray absorption near-edge) and DFT calculations on such a model compound.[105] Both experiments point at the η^2-peroxo ligand as the protonation site, thus supporting the hypothesis that a key role is also being played by a hydroperoxo intermediate in the catalytic cycle of the VHPOs functional model. DFT was in fact used by the same research group to investigate the structural, electronic, and catalytic properties of the vanadium cofactor in VHPOs,[106,107] also as a function of environment and protonation state.[108] These studies demonstrated the important role of protonation in the cofactor activation.

Quite surprisingly, at odds with the common knowledge, there have been a couple of works where a reactivity comparison of two oxo peroxo vanadium complexes with their dioxo reduced counterparts was performed, and the results obtained indicate that the dioxo species is the more active.

In the first case, the reactions analysed are the oxidation with [VO(O$_2$)tpa]PF$_6$ and [VO$_2$tpa]PF$_6$ (tpa = tris-(3-pyridyl)methylamine) of α-terpinene to *p*-cymene and of 2,6-di-*tert*-butyl phenol to quinone.[109]

The other more recent example[110] refers to the oxygen transfer behaviour of [VO(O$_2$)(*t*Bu$_2$bpy)]BF$_4$ and [VO$_2$(*t*Bu$_2$bpy)]BF$_4$ (*t*Bu$_2$bpy = 4,4′-di-*tert*-butylbipyridine) toward hydroquinone, TEMPOH and phosphines.

A critical collection of papers related to the catalytic oxidations with vanadium complexes was published in 2003.[111]

Bromination

In connection with the studies aimed at mimicking the reactivity of VHPOs enzymes, complex **24** has been studied in the oxidative bromination of 1,3,5-trimethoxybenzene (TMB). A 90% yield of BrTMB was obtained in acid conditions, in a short reaction time.

A fast reaction is observed also with triphenylphosphane, while the analogous reaction with methylphenyl thioether is much slower.[40]

Complexes **35** and **36**, characterized by the dimeric triperoxo structure, are fast and efficient oxidants of bromide, thus being mediators of the bromination reaction of organic substrates in an aqueous organic media.[42] Such a dimeric structure resembles the intermediate proposed by Butler[112] in the catalytic cycle of VHPOs mimicking systems. The analogous mononuclear complexes **27** and **28**, are inactive.

Not considering only isolated peroxo complexes, there are vanadium oxo species which, in the presence of H_2O_2, can efficiently act as a functional mimic of VHPOs enzymes. A nice example refers to the V(v) amine triphenolate derivatives (Fig. 3), which brominate 1,3,5-trimethoxybenzene to 2,4,6-trimethoxybromobenzene with yields and TONs up to 92% and 1260, respectively, in acid conditions.[113]
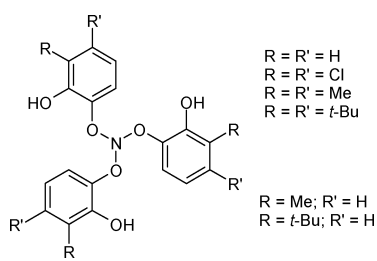

Fig. 3 Triphenolate amine ligands.

Effective mimicking of VHPOs was also obtained by using a tripodal ligand, bis[(1-methylimidazol-2yl)methyl] 2-(pyridyl-2-yl)ethyl amine, bound to a V(v) oxo centre in the presence of hydrogen peroxide.[114] This complex shows a structural similarity with the reduced form of the prosthetic group of VHPOs and resembles their catalytic activity in bromide to bromine oxidation.

The anchoring of peroxovanadates to soluble polymers appears to be a promising field. A recent example[49] shows the activity of supported peroxo species **40** and **41** in bromination of aromatics.

Oxidation of sulfur and nitrogen containing substrates

From the synthetic point of view, the oxidation of prochiral thioethers retains a great significance as a testing reaction for the catalytic activity of chiral non racemic complexes. In such a field, several nice examples of catalysts have been reported, and, specifically with vanadium species, Bolm collected topical reports in 2003.[115] To note, often the synthetically useful procedures do not rely on the use of hydrogen peroxide, as there are alkylhydroperoxides that are much more reactive and selective with the catalysts studied.[116] Clearly, from the sustainable point of view, this should be changed in the near future. An improvement in this area has recently been obtained by Licini and colleagues[113] They reported the use, in turn-over conditions, of vanadium amine triphenolate derivatives as the catalysts in sulfoxidation reactions with H_2O_2. Only an almost quantitative yield of sulfoxide was detected, even in the presence of an equimolar amount of oxidant. Furthermore, the catalyst loading was decreased down to 0.01%, observing TONs and TOFs up to 9900 and 8000 h⁻¹, respectively.[113]

An oxovanadium complex, containing tridentate Schiff bases derived from β-amino alcohols (see Fig. 4), has been tested in the enantioselective oxidation of methyl phenyl sulfide with hydrogen
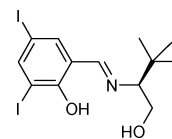

Fig. 4 The Schiff base ligand, efficient in asymmetric catalysis.

peroxide. At low temperature, with an appropriate substitution pattern in the ligand, up to 98% e.e. was obtained. The scope of the reaction was not checked with other substrates.[117]

More recently, the oxidation of sulfur containing substrates is receiving increasing interest, in connection with the search for a sustainable oxidative desulfurization procedure for fuels. In particular, the complete oxidation of difficult to oxidize substrates, such as aromatic sulfides, is still a challenging task, with benzothiophene, dibenzothiophene and their derivatives being the target substrates.

In this respect, the catalytic activity of V and Nb oxoperoxo-complexes, containing a Schiff-base ligand, was analysed in the H_2O_2 oxidation of methyl phenyl sulfide and benzothiophene. V(v) complexes are less reactive but more selective than the corresponding Nb species. However, sulfone was always observed. Benzothiophene was less reactive than methyl phenyl sulfide and dibenzothiophene was not oxidized at all, even at temperatures as high as 70 °C.[118]

Interestingly, a cyclodextrin inclusion compound containing a dioxo-vanadium with a biphenyl-4-carboxylic acid salicylidene hydrazide ligand has been tested as a catalyst for the oxidation of phenyl methyl sulfide.[119] Unfortunately, the catalytic activity of the inclusion compound is not very exciting and almost no e.e. was found.

A similar class of hydrazide ligands has been used to prepare some Mo(VI) dioxo derivatives, which have been proved to be efficient catalysts for the oxidation of sulfides to sulfoxides with H_2O_2.[120]

Also, Mo catalysis in the oxidation of aromatic sulfides is receiving great attention, for its possible application in the oxidative desulfurization of gasoline.[121]

Mono and diperoxo molybdenum complexes, **63** and **75**, containing 8-quinolinol as a ligand, have been used in the oxidations of sulfides with H_2O_2.[70] The reaction is catalytic, reaching TON of about 500. Due to the high reactivity of the peroxo molybdenum species, it is not unexpected that the unselective formation of both sulfoxides and sulfones is observed with aliphatic and aromatic substrates.

A cyclopentadienyl molybdenum acetylide derivative (Fig. 5) has been effectively used in the oxidation of aromatic amines to nitroso derivatives (with substrate conversion >95% and selectivity toward nitroso derivatives from 75 to 99%).[122] In this reaction, the presence of a co-solvent was obviously necessary. Increasing the temperature significantly lowered the selectivity. The electron withdrawing, as well as electron-donating, groups are tolerated in the oxidation of aromatic amines.
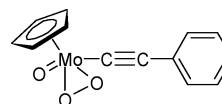

Fig. 5 Mo(VI) acetylide catalyst.

Oxidation of alcohols

The selective oxidation of an alcoholic function is an interesting process, which can be performed also with metal peroxides. Homogeneous procedures, as well as two-phase systems, were proposed in the past.[3,8] The *in situ* prepared oxo diperoxo vanadate has been proposed as a nucleophile and an oxidant in the oxidation of benzyl alcohol or benzyl halides to the corresponding carbonyl compounds.[123] Several different aromatic and aliphatic substrates have been tested and high yields, up to 90%, of the aldehydes or ketones have been detected. In the case of the oxidation of primary and secondary benzyl bromides or chlorides, the reaction has been carried out in water in the presence of a phase transfer agent (*i.e.* Aliquat 336). The reaction mechanism proposed for such a reaction is questionable, considering that acid catalysis is required and it is likely that the protonation of the anionic peroxides occurs before the protonation of the substrate.

A larger number of examples are present in the recent literature concerning the oxidation of alcohols in the presence of Mo catalysts. An effective procedure is based on the use of Mo complexes **63** and **75**, which, in the presence of hydrogen peroxide, catalyse the selective oxidation of several primary and secondary alcohols to the corresponding carbonyl compounds. TONs higher than 800 have been reported. Interestingly, the oxidation of methanol to a mixture of formaldehyde and formic acid was obtained.[70] Such a catalytic system is active also in the oxidation of phenol and amines.

Interesting reports appeared lately reporting solventless alcohol oxidations with H_2O_2, catalysed by Mo(VI) species. In the first example, 1,4-diazabicyclo[2.2.2]octane was used as a ligand.[124] The reaction mixture is composed of the alcohol and a 30% aqueous solution of the oxidant. With benzyl alcohol, a 96% yield of aldehyde was obtained with 98% selectivity. Several differently substituted primary and secondary alcohols were tested (aromatic, aliphatic, cyclic, and acyclic) and in all cases the yields and selectivity approached 96% and 99%, respectively. Even more interesting, is the observation that the catalytic phase can be recycled, without activity loss, thus greatly enhancing the synthetic scope and the sustainability of the procedure.

A similar reactivity has been reported for the cyclopentadienyl molybdenum acetylide derivative of Fig. 5. Such a species activates the hydrogen peroxide, forming, in aqueous solution, a Mo peroxo complex, which selectively oxidizes a series of primary alcohols to the corresponding aldehyde without the need for a co-solvent.[125] Very high conversions of the substrates are obtained, together with a high selectivity toward the aldehyde (> 90%, TON ≈ 400).

Oxidation of alkenes

The selective oxidation of alkenes to the corresponding oxiranes is one of the most important and still challenging reactions, even more problematic being the attainment of enantioselective procedure. This is particularly true when the unsubstituted double bonds are considered.

Several research groups, in the past, reported effective and selective metal catalysed processes with peroxides. In particular, in the presence of d^0 early transition metals, hydrogen peroxide can be the primary oxidant, thus extremely increasing the sustainability of the reaction. A general critical collection of such procedures appeared in the Patai series.[1] To note, several examples of metal peroxides lead to the conversion of the substrate and a selectivity toward epoxides of higher than 90%, so the exploitation of new catalytic systems is actually even more challenging.

Limiting our attention to V and Mo catalysis, the scope of this review, in recent years there have been almost no reports on the use of isolated peroxo complexes. This is clearly to be expected, considering that the catalytic processes that use cheap and "green" primary oxidants, are much more interesting from all points of view. However, in several cases it is observed that the epoxidation reaction with hydrogen peroxide in the presence of V or Mo is much less effective with respect to the reaction performed with alkyl hydroperoxides, in particular with TBHP. Nice recent examples of this reactivity refer to half sandwich Mo cyclopentadienyl complexes[126] and to a supported dioxo Mo species containing tridentate Schiff bases as ligands.[127]

Another example refers to the epoxidation of cyclohexene in the presence of complex **72**.[76] With TBHP as the primary oxidant, significant epoxidation is observed, while in the presence of H_2O_2 no reaction occurred. However, the Mo oxo diperoxo derivative is isolated upon the reaction of the dioxo precursor in the presence of H_2O_2, while any attempt to isolate it from TBHP failed.

A closely related monoperoxo Mo(VI) species, **60**, has been found to be active in the isomerisation of allylic alcohols, while no oxidative behaviour was detected.[67]

Table 4 contains highlights, with selected model substrates, of catalytic epoxidation with hydrogen peroxide, in the presence of different V and Mo precursors.

Interestingly, the reactivity and selectivity obtained with molybdenum catalysts are generally much higher than those obtained with vanadium. This observation is in line with the common knowledge that molybdenum peroxo species are better electrophilic oxidants, with respect to their vanadium containing counterparts. Furthermore, it is known that metal catalysed hydrogen peroxide decomposition is much more efficient when vanadium is used, particularly if radical processes take place.[99]
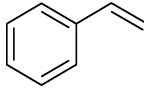
It is noteworthy that some work has been dedicated to the search for new reaction media for catalytic oxidations with H_2O_2, in order to obtain even more sustainable processes. In Table 4, an example is shown related to a reaction with a diperoxo molybdenum in bmimPF$_6$,[81] an ionic liquid that is often used as an alternative to volatile molecular solvents.[131]

Also, complex **75** has been used in ILs to epoxidize, with H_2O_2, a technical mixture of methyl oleate and methyl linoleate in basic conditions. The reaction analysed is significant in view of the utilization of renewable resources. However, the results reported in the presence of the catalyst, the very high conversion of substrates (>90%) with an almost total selectivity towards epoxide, appear to be comparable to those obtained in the presence of hydrogen peroxide and carbonate only.[132]

The use of ILs is now quite well established in metal catalysed oxidation reactions,[133] as well as in many other metal catalysed processes.[131] In several cases, more selective and faster processes have been obtained, in comparison with similar reactions carried out in molecular solvents. ILs are also useful when microwave heating is used.[134]

The utilization of new reaction media, ILs or supercritical CO_2, for metal catalysed oxidations will probably be further explored in the future, with the scope of realizing a more appealing procedure.

Table 4 Epoxidation reactions with hydrogen peroxide in the presence of selected V and Mo catalysts

$$\text{alkene} \xrightarrow[\text{H}_2\text{O}_2]{\text{cat}} \text{epoxide}$$

Alkene	Catalyst	Solvent	$T/^{\circ}C$	Reaction time	% conv.	Selectivity,% (yield,%)					Ref.
						epoxide	1,2-diol	aldehyde	ketone	acid	
cyclohexene	VO(tmbmz)$_2$[a]	MeCN	80	6 h	64.0	2.4	84.7		12.4		128
	PS- VO(tmbmz)$_2$[a,b]	MeCN	80	6 h	86.0	3.2	81.3		14.8		128
	MoO$_2$(tmbmz)$_2$[a]	MeCN	80	6 h	55.0	2.2	85.7		11.1		128
	PS- MoO$_2$ (tmbmz)$_2$[a,b]	MeCN	80	6 h	66.0	2.3	83.4		13.2		128
	[MoO(O$_2$)$_2$(4,4'-bipy)]$_n$[c], 76	CH$_2$Cl$_2$	25–40	4–6 h	85–90	>99					77
	MoO(O$_2$)$_2$(4-MepyO)$_2$[d], 82	bmimPF$_6$[e]	60	18 h	73	>99 (73)					81
cyclooctene	MoCl$_2$(O)$_2$(OPMePh$_2$)$_2$[f]	MeCN	55	24 h	35.0	>99					68
		EtOH	70	6 h	43.0	>99					68
	MoCl$_2$(O)$_2$(dppmO$_2$)[g]	EtOH	70	6 h	26.0	>99					68
	[MoO(O$_2$)$_2$(4,4'-bipy)]$_n$[c], 76	CH$_2$Cl$_2$	25	6 h	40	>99					77
	MoO(O$_2$)$_2$(4-MepyO)$_2$[d], 82	bmimPF$_6$[e]	60	18 h	>90	>90					81
styrene	VO(tmbmz)$_2$[a]	MeCN	80	6 h	65.0	3.6	28.6	66.3			128
	PS- VO(tmbmz)$_2$[a,b]	MeCN	80	6 h	81.0	4.9	29.4	62.6			128
	MoO$_2$(tmbmz)$_2$[a]	MeCN	80	6 h	49.0	3.0	27.0	68.8			128
	PS- MoO$_2$ (tmbmz)$_2$[a,b]	MeCN	80	6 h	68.0	3.1	29.5	66.0			128
	MoO(O$_2$)$_2$(4-MepyO)$_2$[d], 82	bmimPF$_6$[e]	60	18 h	57.0	> 99 (10)					81
	VO(Acpyr^{I})$_2$[h]	MeCN	25	18 h	88.0		15 (13)	62 (55)		23 (20)	129
	VO(Acpyr^{II})$_2$[i]	MeCN	25	18 h	48.8	6 (3)	4 (2)	86 (41)		4 (2)	129
	VO(Acpyr^{IV})$_2$[j]	MeCN	25	18 h	35.0			100 (76)			129
	VO(Acpyr^{V})$_2$[k]	MeCN	25	18 h	84.0		11 (9)	70 (59)		19 (16)	129
	VO(Acpyr^{VI})$_2$[l]	MeCN	25	18 h	90.0		12 (11)	67 (60)		21 (19)	129
	VO(Acpyr^{VII})$_2$[m]	MeCN	25	18 h	85.0		6 (5)	71 (60)		23 (20)	129
	MS-MoO(O$_2$)$_2$(QOH)$_2$[n]	MeCN	25	20 h	98.0	74			24		130
	MS-MoO(O$_2$)$_2$(QO)[n]	MeCN	25	20 h	96.0	76			20		130

[a] tmbmz = 2-thiomethylbenzimidazole. [b] PS = polymer supported. [c] heterogeneous; 4,4'-bipy = 4,4'-bipyridyl. [d] 4-Mepy = 4-methylpyridine; H$_2$O$_2$/urea (UHP) used as the oxidant. [e] bmim = butylmethylimidazolium cation. [f] with H$_2$O$_2$, it forms complex **72**. [g] with H$_2$O$_2$, it forms complex **73**. [h] VO(Acpyr^{I})$_2$ = 1-phenyl-3-methyl-4-terz-butylacetyl-5-pyrazolone. [i] VO(Acpyr^{II})$_2$ = 1,3-dimethyl-4-acetyl-5-pyrazolone. [j] VO(Acpyr^{IV})$_2$ = 1,3-dimethyl-4-(1-naphthoyl)-5-pyrazolone. [k] VO(Acpyr^{V})$_2$ = 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone. [l] VO(Acpyr^{VI})$_2$ = 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone. [m] VO(Acpyr^{VII})$_2$ = 1-(2-pyridyl)-3-methyl-4-trifluoroacetyl-5-pyrazolone. [n] MS = mesoporous silica; QOH = 8-quinolinol.

The cyclopentadienyl molybdenum acetylide[122] derivative is an efficient catalyst in performing the *cis*-dihydroxylation of olefins in the presence of hydrogen peroxide.[135] By using cyclohexene, an interesting conversion of the substrate (95%) and a high selectivity in the formation of the diol was obtained, using *t*-BuOH as the solvent, see Scheme 13. Up to 5 catalytic cycles were obtained, either adding H$_2$O$_2$ stepwise or recycling the catalyst after isolation from the reaction mixture.
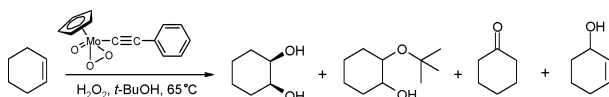
Scheme 13 The *cis*-dihydroxylation of cyclohexene.

(reaction conditions: H$_2$O$_2$, *t*-BuOH, 65 °C)

Oxidation of alkanes

One of the most attractive transformations of organic substrates is the selective oxidation of alkanes in mild conditions. Certainly, the replacement of the nowadays-used harsh industrial oxidation procedures would have a great impact. Truly sustainable and effective processes should make use of dioxygen as the primary oxidant, without the need for a sacrificial reductant and some procedures have been proposed during the years, based on diverse

metals and also on polyoxometallates.[136] The reaction is likely to involve radical intermediates and, therefore, with the metals we are discussing here, the use of the reduced form of the catalyst is necessary (*i.e.* V(IV) complexes). Just as an example, the simple VO(acac)$_2$ has been used in the oxidation of adamantane to 1- and 2-adamantol and 2-adamantanone with dioxygen in acid conditions.[137] Evidence on the occurrence of the peroxo vanadium species has been obtained.

The situation is different if we concentrate on the V(V)/H$_2$O$_2$ systems. In this respect, a breakthrough was obtained, more than twenty-five years ago, by Mimoun, with the synthesis of VO(O$_2$)pic (pic = picolinate), a species that is very active in the hydroxylation of alkanes and aromatics.[138] Subsequently, with a closely related species, Shul'pin reported, in numerous different papers, the oxidation of many diverse hydrocarbons. Just as a recent example, the bis(maltolato) vanadium oxo complex, in the presence of pyrazine-2-carboxylic acid, was used in the oxidation, with H$_2$O$_2$, of cyclohexane to cyclohexyl hydroperoxide and benzene to phenol.[139] Other substrates were also examined, with the aim of determining the selectivity parameters. There were quite low values observed in all the experimental conditions used. To note, when the maltolato precursor was heterogenized on modified silica gel, the catalytic activity was much lower and the selectivity was modified.

Another interesting example refers to the aminebis(phenolate) oxo vanadium(v) complex, Fig. 6. This species, which resembles, as many others do, the VHPOs enzymes active site, is effective in the catalytic oxidation of various methylbenzenes to the corresponding acids and hydroxymethyl benzoic acids.
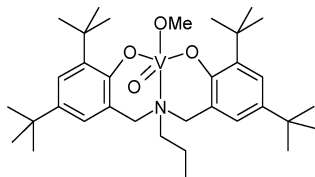

Fig. 6 Oxo vanadium catalyst for the oxidation of methyl benzenes.

The TONs obtained are higher than 130.[140] The authors propose the intermediate formation of a hydroxo-hydroperoxo species as the active oxidant.

In 2008, the catalytic activity of the two oxo vanadium(v) complexes, containing, respectively, salicylhydroximate and 5-chloro salicylhydroximate ligands, were tested in the hydroxylation of aromatic and aliphatic substrates.[141] In the presence of five-fold excesses of hydrogen peroxide, the high conversion of the substrates, with TON up to 360, was achieved. Lower conversions and selectivity were observed with linear alkanes, in comparison with those of cyclohexane, this substrate being the most oxidizable one. Interesting yields and selectivity were observed also with several aromatic substrates.

Conclusions

In this in no way comprehensive review, we hopefully have offered to the scientists interested in catalytic oxidations, an outline, clearly limited to the V(v) and Mo(vi) species, on the recent activity in this field. In doing so, it has been realized that, even though many features of isolated peroxo complexes are elucidated, in many examples the catalysis with them is scarcely explored.

As a personal note, we would like to underline that the research in metal catalyzed oxidation with peroxides will have an even greater future, if and when more efficient and sustainable protocols are established.[142] The adherence to the principles of green chemistry is already assured by the fact that these reactions employ hydrogen peroxide, one of the most sustainable oxidants and a catalyst, which, in several instances, can be reused in subsequent cycles without losing activity.[143] Therefore, much of the work should be devoted firstly to increasing the performance of the catalysts, in terms both of turnover numbers and turnover frequency and secondly, but not with less importance, to the reduction of the environmental impact due to the use of large amounts of harmful volatile organic solvents.

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