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Coordination and hydrogen bonding diversity of OOH ligand in crystalline organoelement and inorganic hydroperoxides

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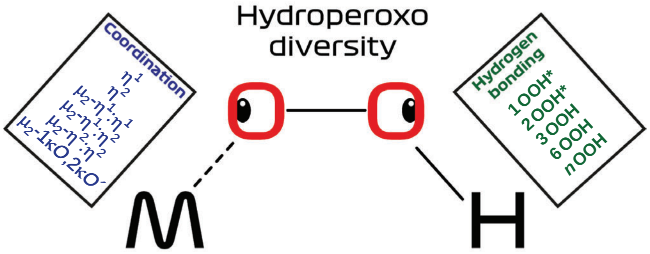
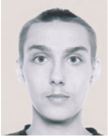
Hydroperoxo complexes, that is coordination compounds with directly bound hydroperoxo ligands OOH$^-$, are encountered and applied in various fields such as catalytic oxygenations and functional material precursors. This focus article spotlights a hydroperoxo ligand as a key moiety providing the reactivity of these complexes and stabilization of their crystal structures through hydrogen bonding. The diversity of hydroperoxo coordination types and hydrogen-bonded motifs is demonstrated for the crystalline organoelement and inorganic hydroperoxides presented in the structural databases.



Keywords: organoelement hydroperoxide, inorganic hydroperoxide, crystal packing, hydroperoxo ligand, coordination mode, hydrogen bonding.



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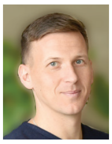

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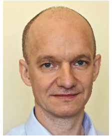

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Introduction

Peroxo compounds are widely utilized as oxidizing agents in the chemical, pulp and paper, textile, medical, animal husbandry and other fields.[1] Hydrogen peroxide is the simplest and most common peroxo compound that is ubiquitous in industry in the form of aqueous solutions or cocrystals with other organic or inorganic molecules, known as peroxosolvates.[2,3] Besides, hydrogen peroxide acidity allows for deprotonation and/or substitution of one or both hydrogen atoms with different nature moieties, explaining the peroxo compound class diversity such as organic peroxides, inorganic peracids, metal peroxides, and peroxo complexes. Hydroperoxides, *i.e.* compounds bearing a hydroperoxo functional group (–O–O–H), constitute the least explored class of peroxo compounds. In addition to the pronounced redox properties characteristic of all peroxides due to the presence of oxygen atoms with an intermediate oxidation state of –1, hydroperoxides have an acidic proton. Furthermore, hydroperoxo compounds are prone to disproportionation with the formation of superoxide derivatives under the action of heating or irradiation in the visible and ultraviolet range.[4,5]

The hydroperoxide class can be subdivided into organic hydroperoxides (ROOH, where R = organic fragment), organoelement and inorganic hydroperoxides (MOOH, where M = p- or d-block element, with/without M–C bond, respectively), as well as ionic hydroperoxides (ammonium hydroperoxide $NH_4^+OOH^-$).[6] The synthesis, reactivity and stability aspects of organic hydroperoxides are reasonably studied as they have long been put into practice both in laboratory and industry.[7] On the contrary, the preparation and application of organoelement and inorganic hydroperoxides are generally significantly hampered by their high chemical activity which is reinforced with the coordination of a hydroperoxo ligand to a Lewis acidic centre rather than simple covalent binding with an organic fragment.[8] According to the latest issues of Cambridge Structural Database (CSD)[9] and the Inorganic Structural Database (ICSD),[10] reliable crystal structures of hydroperoxo complexes account for merely about 2% of the total number of structurally characterized peroxo complexes (24 out of *ca.* 1500). Meanwhile, coordination compounds with hydroperoxo ligands have been instrumental in understanding the mechanisms of various catalytic processes, in particular enzymatic reactions.[11,12] Moreover, these compounds have turned out to be convenient precursors for the various purpose functional materials.[13–16] In this regard, the development of new synthetic approaches to the stabilization, isolation, and characterization of hydroperoxo complexes is an important task of modern coordination chemistry.

We have recently postulated the conditions favorable for the formation of p-block hydroperoxo and alkylperoxo complexes.[17,18] Firstly, the common peroxidation agents, hydrogen peroxide and organic hydroperoxides, should be used in basic media to provide their deprotonation and the subsequent peroxo coordination. Otherwise, these compounds predominantly exist in solution in their undissociated state and are known to be weak ligands not capable of hydroperoxo and peroxo complex formation.[18,19] Secondly, a large excess of concentrated hydrogen peroxide is required to prevent the formation of peroxo-bridged or hydroxo structures by shifting the reaction equilibria. In case of hydrogen peroxide lack, the high hydroperoxide activity is responsible for the further (poly-)condensation to yield the more thermodynamically stable and abundant peroxo complexes, as demonstrated both experimentally and theoretically for several p-block elements, *e.g.* Ge, Te and Sb.[20–22] Besides, dilute hydrogen peroxide solutions would promote the formation of hydroxo rather than hydroperoxo coordination compounds, despite the higher computed stability of the latter in the gas phase.[20,21] The anhydrous (*i.e.* pure) hydrogen peroxide is therefore a relevant form of peroxidation agent, which could be relatively safely obtained from the crystalline serine peroxosolvate.[23] In light of above, a reliable technique to synthesize stable hydroperoxo complexes rests on utilizing organoelement basic precursors, such as trialkyl and triaryl hydroxo compounds, in order to (i) ensure the sufficiently basic conditions without additional agents, and (ii) prevent polycondensation due to the organoelement fragments (*i.e.* M–C bonds) resistant to substitution.[4]

As for the hydroperoxo coordination compounds of d-block elements, they are frequently encountered as labile intermediates in metal-catalyzed oxidation reactions rather than subject to intentional isolation. Nevertheless, a number of complexes were prepared by different techniques, including protonation of peroxo congeners,[24,25] hydrometalation with dioxygen,[26,27] and simple hydrogen peroxide treatment.[28,29] The appropriate synthesis method and thermal stability of the complex largely depend on the transition metal nature and its electronic and steric environment. For example, certain hydroperoxo coordination compounds of redox-inactive Rh^{III}, Pd^{II} and Pt^{IV} remain robust at room or slightly elevated temperature,[27,30,31] in contrast to nickel complexes, susceptible to decomposition or further oxidation.[32] Additionally, shielding role of sterically hindered ligands[28,33,34] and absence of coordinating anions[25] were marked as essential stabilizing factors of several complexes under ambient conditions. Last but not least, hydroperoxo groups inevitably participate in hydrogen bonding with each other and/or with other neighboring ligands, solvent molecules and anions, owing to the presence of both proton-donor and two proton-acceptor sites.[35] While hydrogen bond formed as proton donor seems to favor the complex stabilization, those formed as proton acceptor may have opposite effects relying on the association mode, bringing vital differences in metalloprotein and biomimetic catalysis, as described below.[33]

This brief review aims to summarize the findings on organoelement and inorganic hydroperoxides with the emphasis on crystalline compounds characterized with single-crystal X-ray diffractometry (SCXRD). The coordination types of hydroperoxo ligands in crystal structures of p- and d-block element complexes presented in the structural databases are discussed. To the best of our knowledge, no structural data is available for lanthanide and actinide hydroperoxo complexes, even though hydroperoxo coordination by f-block elements was also reported.[36] The diversity of all currently known hydrogen-bonded motifs (HBMs) of hydroperoxo ligands is demonstrated and exemplified by specific crystal structures. Finally, the most prominent instances of organoelement and inorganic hydroperoxide occurrence and application in catalysis and material chemistry are summarized.

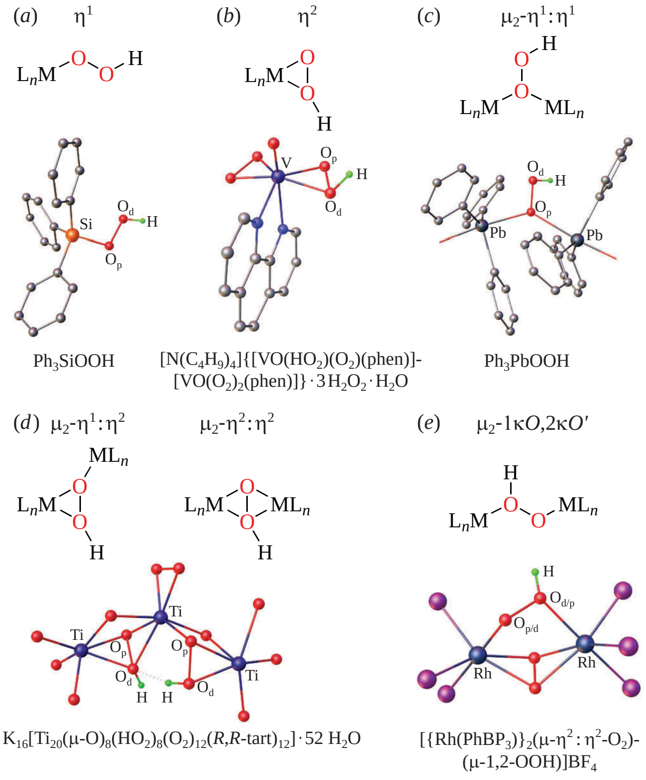
Coordination diversity of hydroperoxo ligands

Recently, we have witnessed the confusion between superoxo, O_2^-, and hydroperoxo, OOH^-, species in previously reported aluminum and tin compounds.[4,14] That is not surprising and is sometimes the case because these ligands bear the same negative charge (–1) and may appear similar while resolving the crystal structures of the quality not sufficient to localize the dioxygen-bound hydrogen atom. The correct dioxygen ligand form assignment is essential to identify the actual structure of the examined systems. It was demonstrated that the photolytically induced hydroperoxo ligand disproportionation leads to the coordination of superoxo moieties even for p-block elements,[4] let alone transition metals, frequently catalytically active for the hydrogen peroxide decomposition and capable of incorporating both superoxo and hydroperoxo forms of the dioxygen ligand. In order to disambiguate, structural studies can furnish the representative O–O bond lengths of dioxygen fragments and distances of potential hydrogen bonds, along with hydroperoxo group proton objective localization from Fourier difference synthesis and subsequent position refinement. In addition, complementary spectral studies by EPR, NMR, MS, FTIR and Raman techniques would be relevant and helpful to confirm the correct assignment of the hydroperoxo ligand.

In this regard, the crystal structures of hydroperoxo complexes presented in the CSD and the ICSD and the corresponding original publications have been critically analyzed for reliability of the experimental results claiming the hydroperoxo ligand formation. The structures have therefore been categorized into three groups: (**I**) hydroperoxides with objectively localized protons; (**II**) hydroperoxides with geometrically located protons and hydroperoxo form confirmed by other experimental techniques; (**III**) hydroperoxides with geometrically located protons, involving erroneous or ambiguous crystal structure solution or refinement (*e.g.* severe disorder, large thermal ellipsoids) and/or no hydroperoxo form confirmation by other experimental techniques, as well as hydroperoxides with not localized protons. Since compounds in the group **III** suffer from the lack of reliable structure confirmation, below we discuss in detail the structural parameters of hydroperoxo ligands of p- and d-block element hydroperoxo complexes from the groups **I** and **II** only. In compliance with structural and spectral data, hydroperoxo complexes feature different types of hydroperoxo coordination, illustrating the coordination diversity of a hydroperoxo ligand (Figure 1).

Hydroperoxo complexes of p-block elements

To date, the CSD and the ICSD contain reliable structural data about 13 p-block element hydroperoxides (Table 1). This is an order of magnitude less than that of structurally characterized coordination compounds of p-block elements with peroxo ligands (>130 entries). Within formula units, the hydroperoxo ligands are coordinated to central atoms in the quantities of one (B, Si, Ge, Sn, Pb),[4,14,17,37,38] two (Sb)[22] or six (Sn).[39] Notably, the anionic tin complex $Cs_2Sn(OOH)_6$ is hitherto the sole homoleptic hydroperoxo coordination compound with complete structural characterization, among both transition and non-transition elements.[39] With the exception of this and two another tin inorganic complexes,[14,40] as well as two boron complexes featuring B–F and/or B–N bonds,[37,38] the rest of the compounds in Table 1 are trialkyl or triaryl derivatives, thus being organoelement ones.



Ph_3SiOOH

$[N(C_4H_9)_4]\{[VO(HO_2)(O_2)(phen)]$-$[VO(O_2)_2(phen)]\} \cdot 3H_2O_2 \cdot H_2O$

Ph_3PbOOH

$K_{16}[Ti_{20}(\mu\text{-}O)_8(HO_2)_8(O_2)_{12}(R,R\text{-tart})_{12}] \cdot 52\ H_2O$

$[\{Rh(PhBP_3)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2)$-$(\mu\text{-}1,2\text{-}OOH)]BF_4$

Figure 1 Schematic representation of different types of hydroperoxo ligand coordination and the corresponding examples of crystal structure fragments. Hydrogen atoms other than those of hydroperoxo ligands were omitted for clarity. In (*d*), potassium cations in the structure were omitted for clarity.

In all the crystal structures considered, the end-on (η^1) hydroperoxo coordination type is observed [Figure 1(*a*)],[17] characterized by the M–O_d separation substantially exceeding the M–O_p bond distance and obtuse M–O_p–O_d angle (O_p and O_d are proximal and distal oxygen atoms of a hydroperoxo ligand, respectively). However, the crystal structure of triphenyllead hydroperoxide is peculiar due to the bridging hydroperoxo ligand, coordinating in the μ_2-η^1:η^1 fashion [Figure 1(*c*)] and allowing for the formation of 1D coordination hydroperoxo polymer, that is infinite $[Ph_3PbOOH]_n$ chains.[4]

Based on the M–O_p–O_d–H torsion angles, the vast majority of hydroperoxo ligands exhibit anticlinal conformations (*cf.* 90.2° in crystalline hydrogen peroxide).[41] The average O_p–O_d bond distance is equal to 1.476 Å (26 entries), slightly greater than found in solid hydrogen peroxide [1.461(3) Å],[39] which is in agreement with generally experimentally observed small bathochromic shifts of ν(O–O) bands in FTIR and Raman spectra.[4,14,17,22,39] Moreover, average O_p–O_d bond distance and O_p–O_d–H angle (98°) are reminiscent of those in ionic ammonium hydroperoxide [1.4953(6) Å and 103.6(6)°], in which a hydroperoxo moiety is not exposed to any coordination centre.[6] Taken together, this could serve as an exemplary hydroperoxo ligand structural characterization.

Hydroperoxo complexes of d-block elements

As for d-block element hydroperoxo complexes, the structural databases currently provide only 11 trustworthy entries (Table 2). Such crystallographic paucity compared with a plethora of well-known transition metal peroxo complexes is presumably a consequence of trapping and characterization complexity. Among these crystal structures, a square planar palladium complex with two saturated *N*-heterocyclic carbene (NHC) and two hydroperoxo ligands is the sole compound with more than one hydroperoxo ligand at the same coordination centre.[42] On the whole, platinum-group metal complexes occupy virtually a half of the considered compounds.

A similar trend in terms of hydroperoxo coordination type is observed since OOH^- exhibits the end-on fashion in most of the structures. Particularly, the end-on coordination is implemented in dicopper and dimolybdenum complexes with a bridging hydroperoxo ligand (μ_2-η^1:η^1), relative each metal atom.[33,34,43] As determined spectroscopically, a dirhodium peroxo/hydroperoxo complex with interconvertible isomers in solution is specified by an unprecedented hydroperoxo coordination type μ_2-1κ*O*,2κ*O′* [Figure 1(*e*)], although a hydroperoxo hydrogen atom was not localized with SCXRD.[25] Altogether, the preference of the end-on (η^1) over side-on (η^2) hydroperoxo arrangement could be explained with enhanced reactivity of the latter due to a stronger metal activation and better steric accessibility which prevent isolation of η^2-OOH containing species.[44] However, these were found in the three structurally characterized complexes of vanadium and titanium, resulting in η^2 [Figure 1(*b*)] or μ_2-η^1:η^2 and μ_2-η^2:η^2 [Figure 1(*d*)] hydroperoxo coordination modes.[29,45,46] It should be noted that the side-on coordination type is characteristic of peroxo and alkylperoxo complexes of these early transition metals, unless steric strain-inducing

Table 1 Coordination type (OOH) and geometrical parameters of unique coordinated hydroperoxo ligands in crystal structures of p-block element hydroperoxo complexes (general formula $\mathrm{M{-}O_p{-}O_d{-}H}$).[a]

No.	Element **M** (database identifier)	OOH	$d(\mathrm{M{-}O_p})$/Å	$d(\mathrm{M{-}O_d})$/Å	$\angle(\mathrm{M{-}O_p{-}O_d})$/deg	$\angle(\mathrm{M{-}O_p{-}O_d{-}H})$/deg	$d(\mathrm{O_p{-}O_d})$/Å	$\angle(\mathrm{O_p{-}O_d{-}H})$/deg	Reference
	(**I**) Crystal structures with objectively localized hydrogen atoms of hydroperoxo ligands								
1	BODIPY-OOH · H_2O								
	B (OTIFOP)	η^1	1.458(2)	2.360(2)	107.70(9)	110(1)	1.465(1)	97(1)	38
2	Ph_3SiOOH								
	Si (ZUHXOS)	η^1; η^1	1.693(1); 1.693(1)	2.547(1); 2.514(1)	106.5(1); 104.63(9)	136(2); –122(2)	1.481(2); 1.479(2)	94(2); 96(2)	17
3	Ph_3GeOOH								
	Ge (ZUHYAF)	η^1; η^1	1.840(2); 1.831(2)	2.651(2); 2.613(2)	105.9(2); 104.1(1)	139(3); –115(3)	1.470(4); 1.471(3)	97(3); 90(3)	17
4	$Cs_2Sn(OOH)_6$								
	Sn (ICSD 260828)	η^1	2.076	2.947	110.8	96.1	1.482	96.8	39
5	$Me_3Sb(OOH)_2 \cdot H_2O$								
	Sb (NILTAH)	η^1, η^1	2.097(2), 2.076(2)	2.867(2), 2.866(3)	105.1(2), 106.5(2)	–108(2), –116(3)	1.483(3), 1.473(3)	99(2), 105(3)	22
6	(p-Tol)$_3$Sb(OOH)$_2$								
	Sb (NILTEL)	η^1, η^1; η^1, η^1	2.067(3), 2.072(3); 2.054(3), 2.068(3)	2.889(3), 2.862(3); 2.927(3), 2.821(3)	107.7(3), 105.7(3); 111.0(3), 103.8(2)	–125(3), –129(4); –123(4), 121(4)	1.486(6), 1.493(6); 1.474(6), 1.488(6)	97(3), 99(4); 89(4), 101(3)	22
7	$Ph_3Sb(OOH)_2 \cdot 2\,MeOH$								
	Sb (NILWEO)	η^1	2.072	2.880	107.2	115	1.481(2)	101(2)	22
8	(p-Tol)$_3$Sb(OOH)$_2 \cdot 2\,$THF								
	Sb (NILWIS)	η^1, η^1	2.068(2), 2.043(2)	2.848(2), 2.775(2)	105.5(1), 102.6(1)	131(2), 137(2)	1.482(3), 1.486(2)	100(2), 98(2)	22
9	$Me_3Sb(OOH)_2$								
	Sb (NIMLAA)[b]	η^1, η^1	2.091(3), 2.093(3)	2.848(3), 2.828(6)	104.3(2), 105.5(3)	103(5), 134.5	1.485(3), 1.422(8)	98(5), 109.4	22
10	$Ph_3Sb(OOH)_2 \cdot 0.75\,THF$								
	Sb (NIMLEE)	η^1, η^1; η^1, η^1; η^1, η^1	2.057(4), 2.078(4); 2.074(4), 2.062(4); 2.074(3), 2.067(3)	2.872(4), 2.849(5); 2.862(5), 2.886(4); 2.830(3), 2.846(3)	107.4(2), 105.2(3); 105.4(2), 108.4(2); 103.8(2), 105.6(2)	–117(3), –132(3); –146(4), –130(3); –123(4), –138(3)	1.482(4), 1.478(5); 1.497(5), 1.470(5); 1.494(5), 1.479(6)	104(3), 96(3); 104(4), 102(3); 98(4), 99(3)	22
11	Ph_3PbOOH								
	Pb (WEBPOM)	μ_2-$\eta^1 : \eta^1$	2.310(3), 2.447(3)	3.119(5), 3.347(5)	110.0(3), 116.1(3)	–161(6), 26(6)	1.450(6)	92(6)	4
	(**II**) Crystal structures with geometrically located hydrogen atoms of hydroperoxo ligands and hydroperoxo form confirmation by other experimental techniques								
12	(L)BOOH (L = 5,10,15-triphenylsubporphyrinato)								
	B (MAJROH)	η^1	1.468(2)	2.369(2)	107.5(1)	–	1.469(2)	–	37
13	$BaSn(OH)_3(OOH)(OO)$								
	Sn (CCDC 1988718)	η^1	2.040	2.629	96.6	–	1.454	–	14
	(**III**) Crystal structures that are untrustworthy for the hydroperoxo form structural confirmation								
14	$Rb_2Sn(OOH)_6$								
	Sn (ICSD 96101)	η^1	2.062	2.800	108.3	–	1.353	–	40

[a] In case of disorder, the data on geometrical parameters are presented considering the positions with the highest occupancy values. The data on $\mathrm{M{-}O_p{-}O_d{-}H}$ torsion angles and $\mathrm{O_p{-}O_d{-}H}$ angles are only provided for the crystal structures with objectively localized hydrogen atoms of hydroperoxo ligands (group **I**). The data on unique hydroperoxo ligands located at the same coordination centre or concerning bridging hydroperoxo ligand are separated by ‘,’ symbol, otherwise by ‘;’ symbol. [b] O_d and H atoms are disordered with 0.520 occupancy.

substituents are present.[47–49] Thus, in the above structures the protonation mostly does not change a common binding mode (as opposed to, for instance, model haem species)[50] and does not lead to the generally expected $\mathrm{O{-}O_H}$ bond shortening, compared with the nearby peroxo moiety within the same complexes.[51] The overall mean $\mathrm{O_p{-}O_d}$ distance is 1.462 Å (12 entries).

Hydrogen-bonded motifs of hydroperoxo ligands

Herein we examine the hydrogen bonding in the crystal structures of hydroperoxo complexes from group **I** only (Table 3). With the exception of two cases of non-conventional $\mathrm{O_d{-}H{\cdots}\pi}$ hydrogen bonds,[4,32] the proton acceptor is well-defined to yield the representative geometrical parameters. The mean $\mathrm{O_d{\cdots}O}$ distance is equal to 2.752 Å (26 entries, see Figure 2 for a distribution), which is about the same found for a sizeable group of crystalline peroxosolvates (2.745 Å).[3] The average $\mathrm{O_d{-}H{\cdots}O}$ angle is 162°.

Theoretically, a hydroperoxo group can accept up to four hydrogen bonds. However, in most of the unique –OOH moieties considered herein O_p atoms act as the single-proton acceptor, interacting predominantly with other hydroperoxo ligands. This is in line with previous investigations of hydroperoxo coordination compounds claiming the stabilization of hydroperoxo species by hydrogen bonding with the proximal oxygen atoms O_p.[28,61,62] By contrast, accepting a proton from

Table 2 Coordination type (OOH) and geometrical parameters of unique coordinated hydroperoxo ligands in crystal structures of d-block element hydroperoxo complexes (general formula M–O_p–O_d–H).[a]

No.	Element **M** (database identifier)	OOH	$d(\text{M–O}_\text{p})$/Å	$d(\text{M–O}_\text{d})$/Å	$\angle(\text{M–O}_\text{p}\text{–O}_\text{d})$/deg	$\angle(\text{M–O}_\text{p}\text{–O}_\text{d}\text{–H})$/deg	$d(\text{O}_\text{p}\text{–O}_\text{d})$/Å	$\angle(\text{O}_\text{p}\text{–O}_\text{d}\text{–H})$/deg	Reference
	(**I**) Crystal structures with objectively localized hydrogen atoms of hydroperoxo ligands								
15	Lig_PhNi(OOH) (Lig_Ph = phenyl-substituted pincer ligand)								
	Ni (HOTREP)	η^1	1.845(2)	2.706(2)	107.9(1)	–90(3)	1.492(2)	101(3)	32
16	[Cu(bppa)(OOH)]ClO_4 (bppa = bis(6-pivalamide-2-pyridylmethyl)(2-pyridylmethyl)amine)								
	Cu (NOBCIQ)	η^1	1.888(4)	2.825(4)	114.5(3)	–60(5)	1.459(6)	102(5)	28
17	($^{\text{Bu}^\text{t}}$PCP)Pd(OOH) ($^{\text{Bu}^\text{t}}$PCP = [1,3-$(\text{CH}_2\text{PBu}^\text{t}_2)_2\text{C}_6\text{H}_3]^-$)								
	Pd (RECKUG)	η^1	2.074(3)	2.898(3)	108.5(2)	164(2)	1.469(4)	98(2)	26
18	$\text{Tp}^{\text{Me}_2}\text{PtMe}_2$(OOH) ($\text{Tp}^{\text{Me}_2}$ = hydrotris(3,5-dimethylpyrazolyl)borato)								
	Pt (GULKED)	η^1	1.980(5)	2.851(5)	110.0(2)	133.9	1.481(5)	109.5	27
	(**II**) Crystal structures with geometrically located hydrogen atoms of hydroperoxo ligands and hydroperoxo form confirmation by other experimental techniques								
19	$(\text{NBu}_4)\{[\text{VO}(\text{HO}_2)(\text{O}_2)(\text{phen})][\text{VO}(\text{O}_2)_2(\text{phen})]\}\cdot 3\text{H}_2\text{O}_2\cdot\text{H}_2\text{O}$ (phen = 1,10-phenanthroline)								
	V (CELNIS)	η^2	1.875(3)	1.956(3)	70.2(2)	–	1.480(4)	–	45
20	Co(BDPP)(OOH) (H_2BDPP = 2,6-bis((2-(*S*)-diphenylhydroxylmethyl-1-pyrrolidinyl)methyl)pyridine)								
	Co (HADZAQ)	η^1	1.900(2)	2.856(2)	113.9(1)	–	1.496(3)	–	52
21	[L(MeCN)Co(OOH)]$(\text{ClO}_4)_2\cdot$MeCN (L = *meso*-5,7,7,12,14,14-Me_6-[14]aneN_4)								
	Co (QORKEN)	η^1	1.878(3)	2.814(3)	117.7(2)	–	1.397(4)	–	53
22	$[\text{L}^\text{et}\text{Cu}_2(\text{OOH})](\text{OTf})(\text{BPh}_4)\cdot$EtCN ($\text{L}^\text{et}$ = ethylene-bridged pyrazolate/triazacyclononane hybrid ligand)								
	Cu (RUKREW)	μ_2-η^1:η^1	1.981(2), 1.992(2)	2.901(2), 3.007(2)	114.0(1), 120.3(1)	–	1.462(3)	–	34
23	*trans*-[Rh(OOH)(Cl)(4-C_5F_4N)(CNBu$^\text{t}$)$(\text{PEt}_3)_2$]								
	Rh (TAYLAH)	η^1	2.025(2)	2.899(3)	110.3(2)	–	1.487(4)	–	24
24	*trans*-[Pd(SIPr)$_2$(OOH)$_2$] (SIPr = 1,3-bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene)								
	Pd (ATIKOE)	η^1, η^1	2.017(2), 1.992(2)	2.826(2), 2.823(2)	110.6(1), 109.1(1)	–	1.392(3), 1.452(3)	–	42
25	*trans*-Pt$(\text{PEt}_3)_2$(Cl)(OH)(OOH)(*p*-CF_3Ph)								
	Pt (TITLIT)	η^1	2.103(4)	2.958(4)	110.4(2)	–	1.472(5)	–	54
	(**III**) Crystal structures that are untrustworthy for the hydroperoxo form structural confirmation								
26	$\text{K}_{16}[\text{Ti}_{20}(\mu\text{-O})_8(\text{HO}_2)_8(\text{O}_2)_{12}$(*R*,*R*-tart)$_{12}]\cdot 52\text{H}_2\text{O}$ (H_4tart = tartaric acid)								
	Ti (HIRPAC)	μ_2-η^2:η^2; μ_2-η^1:η^2	2.05(1), 2.06(1); 2.06(1), 2.02(1)	2.14(1), 1.96(1); 2.72(1), 1.90(1)	72.0(6), 64.4(5); 99.6(7), 63.6(5)	–	1.51(1); 1.46(1)	–	29
27	(Hbipy)[H{VO$(\text{O}_2)_2$bipy}$_2$]$\cdot x\text{H}_2\text{O}_2\cdot(6-x)\text{H}_2\text{O}$ ($x \approx 0.5$, bipy = 2,2′-bipyridine)								
	V (CEYXOT)[b]	η^2	1.893	1.995	71.5	–	1.470	–	46
28	$[\text{Ni}_4(\text{O}\cap\text{O})_4(\text{OMe})_4(\text{OOH})_4]$ (O∩O-bidentate ligand = 4,4,4-trifluoro-1-phenylbutane-1,3-dione)								
	Ni (KURDAF)	μ_3-η^1:η^1:η^1; μ_3-η^1:η^1:η^1; μ_3-η^1:η^1:η^1; μ_3-η^1:η^1:η^1	2.069(6), 2.054(7), 2.067(5); 2.060(5), 2.071(7), 2.050(5); 2.064(7), 2.058(5), 2.060(5); 2.063(5), 2.043(5), 2.058(7)	3.06(1), 3.001(9), 3.076(7); 3.095(9), 3.07(1), 3.02(1); 3.03(1), 3.08(1), 3.07(1); 3.092(9), 3.01(1), 3.03(1)	121.1(5), 117.8(5), 122.1(5); 122.8(5), 120.1(5), 118.4(5); 118.2(5), 121.5(5), 121.3(5); 122.6(5), 118.5(5), 118.5(5)	–	1.430(9); 1.45(1); 1.45(1); 1.44(1)	–	55
29	$[\text{Cu}_2(\text{L})_2(\text{OOH})(\text{OH})](\text{BPh}_4)_2\cdot 5\text{Me}_2\text{CO}\cdot 3\text{H}_2\text{O}$ (L = tris(1-methyl-2-phenyl-4-imidazolylmethyl)amine)								
	Cu (MAMTEA)[c]	μ_2-η^1:η^1	1.942(5), 1.918(5)	2.96(1), 3.05(1)	122.3(5), 131.0(5)	–	1.43(1)	–	33
30	$(\text{pyH})_2[\text{MoO}(\text{O}_2)_2(\text{OOH})]_2$ (py = pyridine)								
	Mo (PYPOMO10)	μ_2-η^1:η^1	2.047, 2.390	2.839, 3.32	107.0, 117.2	–	1.458	–	43
31	[($\text{Tp}^{\text{Pr}^\text{i}_2}$)Rh(OOH)(pz)(pzH)] ($\text{Tp}^{\text{Pr}^\text{i}_2}$ = hydrotris(3,5-diisopropylpyrazolyl)borato, pzH = pyrazole)								
	Rh (CIQPUN)	η^1	1.994(4)	2.898(6)	115.5(4)	–	1.413(8)	–	56
	Rh (CIQPUN01)	η^1	1.997(4)	2.898(6)	115.4(4)	–	1.412(8)	–	30
32	$[\{\text{Rh}(\text{PhBP}_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-O}_2)(\mu\text{-1,2-OOH})]\text{BF}_4$ ($[\text{PhBP}_3]^-$ = tris(methylenediphenylphosphane)phenylborato)								
	Rh (GIYNIM)	μ_2-1κ*O*,2κ*O′*	2.134(3), 2.046(3)	2.931(3), 2.821(3)	108.2(2), 106.4(2)	–	1.450(4)	–	25
33	$[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\mu\text{-pz})_3\text{Rh}(\text{OOH})(\text{dppe})]\text{BF}_4$ (dppe = 1,2-bis(diphenylphosphino)ethane)								
	Rh (LEHZON)	η^1	2.020(5)	2.903(7)	113.4(4)	–	1.431(8)	–	57

Table 2 (continued).

No.	Element **M** (database identifier)	OOH	$d(\mathrm{M–O_p})$/Å	$d(\mathrm{M–O_d})$/Å	$\angle(\mathrm{M–O_p–O_d})$/deg	$\angle(\mathrm{M–O_p–O_d–H})$/deg	$d(\mathrm{O_p–O_d})$/Å	$\angle(\mathrm{O_p–O_d–H})$/deg	Reference
34	$(\mathrm{Tp^{Pr^i_2}})(\mathrm{Ph_3P})\mathrm{Pd(OOH)}$								
	Pd (RAVKOO01)	η^1	1.981(6)	2.829(7)	109.5(5)	–	1.46(1)	–	31
35	*trans*-$[\mathrm{Pd(IPr)_2(OOH)(OH)}]$ (IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene)								
	Pd (YESHOW)	η^1	2.010(3)	2.893(5)	111.7(3)	–	1.466(7)	–	58
36	$\mathrm{Ir_2^{II,II}(tfepma)_2(CNBu^t)_2Cl_3(OOH)}$ (tfepma = $\mathrm{MeN[P(OCH_2CF_3)_2]_2}$)								
	Ir (IBEZIA)[d]	η^1	2.01(3)	3.03(1)	118(1)	–	1.51(3)	–	59
37	$\mathrm{(tmeda)Pt(OOH)(OMe)(Me)_2}$ (tmeda = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine)								
	Pt (MOSFAB)[e]	η^1	2.01(1)	2.92(1)	113(1)	–	1.48(2)	–	60

[a] In case of disorder, the data on geometrical parameters are presented considering the positions with the highest occupancy values. The data on $\mathrm{M–O_p–O_d–H}$ torsion angles and $\mathrm{O_p–O_d–H}$ angles are only provided for the crystal structures with objectively localized hydrogen atoms of hydroperoxo ligands (group **I**). The data on unique hydroperoxo ligands located at the same coordination centre or concerning bridging hydroperoxo ligand are separated by ‘,’ symbol, otherwise by ‘;’ symbol. [b] H atoms are disordered with equal occupancies. [c] $\mathrm{O_d}$ atoms are disordered with equal occupancies. [d] $\mathrm{O_p}$, $\mathrm{O_d}$ and H atoms are disordered with equal occupancies. [e] $\mathrm{O_p}$, $\mathrm{O_d}$ and H atoms are disordered with 0.508(9)/0.492(9) occupancy ratio.

neighboring ligands by an $\mathrm{O_d}$ atom predisposes, albeit not consistently,[30,56] to the hydroperoxo group destabilization or activation.[62–64] The above bears crucial biological implications in metalloproteins and their synthetic analogues (*vide infra*). For comparison, the formation of hydrogen bonds as proton acceptor is not common for crystalline adducts of organic hydroperoxides.[35]

The implemented hydrogen-bonded motifs (HBMs) can be classified according to the number of hydroperoxo ligands engaged in hydrogen bonding with each other and/or with other neighboring ligands (L), solvent molecules and anions (S), within each unique isolated crystal structure fragment (Figure 3). In the absence of nearby hydroperoxo ligands, other moieties (*e.g.* electronically dense phenyl ring) furnish the necessary local hydrogen bonding environment, resulting in two variations of a monohydroperoxo HBM [1OOH·L and 1OOH·L·S, Figures 3(*a*) and 3(*b*), respectively].[4,28] A dihydroperoxo HBM (2OOH), *i.e.* combination of two hydroperoxo ligands into a centrosymmetric dimer as a six-membered ring [Figure 3(*c*)], is the most common hydrogen bonding arrangement.[26] Such hydrogen-bonded cycle can be destroyed [2OOH·S, Figure 3(*d*)] by binding to a proton-accepting solvent molecule (THF)[22] or extended [2OOH·2S, Figure 3(*e*)] *via* accommodating two protic solvent molecules (*e.g.* $\mathrm{H_2O}$).[38] The sole representatives of trihydroperoxo (3OOH) and hexahydroperoxo (6OOH) HBMs are $\mathrm{Ph_3Sb(OOH)_2\cdot 0.75(THF)}$ and $\mathrm{Cs_2Sn(OOH)_6}$, respectively.[22,39] The former motif is an eight-membered ring consisting of two head-to-tail and one head-to-head hydroperoxo linkages [Figure 3(*f*)], whereas the latter is an association of two adjacent hexahydroperoxostannate anions by six hydrogen bonds, each being formed by $\mathrm{O_d}$-H proton donor of one anion and $\mathrm{O_p}$ proton acceptor of another anion [Figure 3(*g*)]. Finally, such head-to-tail hydrogen bonding of hydroperoxo ligands can also give infinite chains [Figure 3(*h*)], denoted as polyhydroperoxo HBM (*n*OOH). The combinations of this motif and 2OOH or 2OOH·2S HBMs in the crystal structures of $\mathrm{Me_3Sb(OOH)_2}$ or $\mathrm{Me_3Sb(OOH)_2\cdot H_2O}$, respectively, provide 3D supramolecular networks.[22]

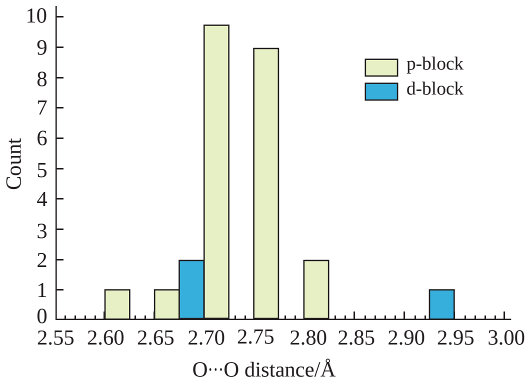


Figure 2 Distribution of O···O distances of hydrogen bonds formed by hydroperoxo ligands as proton donor in the crystal structures of p- (light green) and d-block (light blue) element hydroperoxo complexes (group **I**).

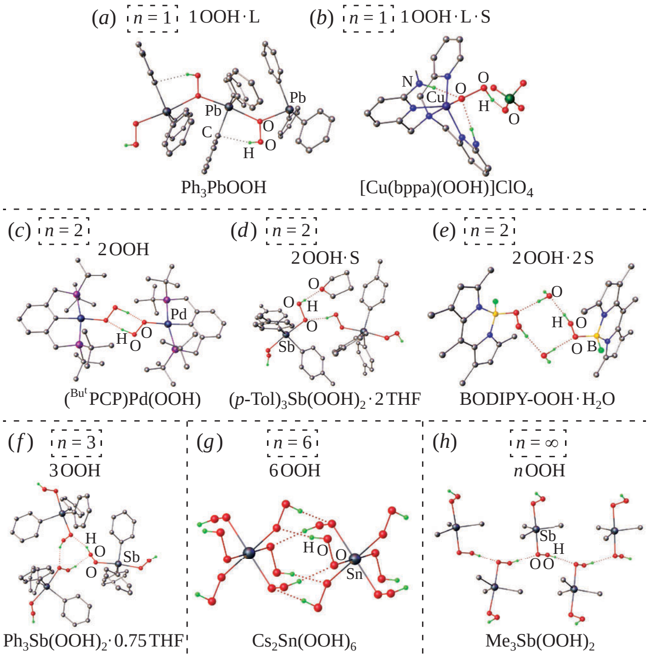


Figure 3 Hydrogen-bonded motifs (HBMs) found in hydroperoxo complexes (group **I**) and the corresponding examples of crystal structure fragments. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonding were omitted for clarity. In (*g*), caesium cations in the structure were omitted for clarity.

Applications of hydroperoxo complexes

Hydroperoxo complexes have been known to be reactive species occurring in transition-metal-catalyzed activation of dioxygen and hydrogen peroxide in synthetic oxidations (Figure 4).[65–68] Apart from the occasional characterization in the solid state (see Table 2), the experimental evidence for their existence predominantly represents identification in solution with spectroscopic methods.[69] Both electrophilic and nucleophilic characters towards organic (*e.g.* olefins, arenes, aldehydes) and inorganic (*e.g.* water, protons, halide ions) substrates were observed, depending on the ligand environment and metal nature and spin state.[70,71] Of particular interest are the investigations

Table 3 The hydrogen-bonded motif (HBM), geometrical and energetic parameters of unique hydrogen bonds formed in the crystal structures of p- and d-block element hydroperoxo complexes (group **I**) as proton donor (general formula M–O_p–O_d–H, proton-accepting site O).[a]

No.	Element **M** (database identifier)	HBM	O	$d(O_d\cdots O)$/Å	$\angle(O_d–H\cdots O)$/deg	E_{HB}/kJ mol^{-1}	Reference
p-block element hydroperoxo complexes							
1	BODIPY-OOH · H_2O						
	B (OTIFOP)	2 OOH · 2 S	O (H_2O)	2.741(2)	171(2)	N/A	38
2	Ph_3SiOOH						
	Si (ZUHXOS)	2 OOH	O (–$\underline{\text{O}}$OH)	2.767(2)	162(3)	31.4–31.8	17
		2 OOH	O (–$\underline{\text{O}}$OH)	2.755(2)	157(3)		
3	Ph_3GeOOH						
	Ge (ZUHYAF)	2 OOH	O (–$\underline{\text{O}}$OH)	2.726(3)	160(4)	31.8–32.5	17
		2 OOH	O (–$\underline{\text{O}}$OH)	2.738(3)	164(4)		
4	$Cs_2Sn(OOH)_6$						
	Sn (ICSD 260828)	6 OOH	O (–$\underline{\text{O}}$OH)	2.642(2)	171(4)	N/A	39
5	$Me_3Sb(OOH)_2 \cdot H_2O$						
	Sb (NILTAH)	2 OOH · 2 S	O (H_2O)	2.817(6)	166(4)	N/A	22
		n OOH	O (–$\underline{\text{O}}$OH)	2.732(4)	173(4)		
6	(*p*-Tol)$_3$Sb(OOH)$_2$						
	Sb (NILTEL)	2 OOH	O (–$\underline{\text{O}}$OH)	2.753(5)	157(5)	N/A	22
			O (–$\underline{\text{O}}$OH)	2.723(5)	154(5)		
		2 OOH	O (–$\underline{\text{O}}$OH)	2.763(5)	162(7)		
		2 OOH	O (–$\underline{\text{O}}$OH)	2.720(5)	150(5)		
7	$Ph_3Sb(OOH)_2 \cdot 2\,MeOH$						
	Sb (NILWEO)	2 OOH · 2 S	O (MeOH)	2.693(2)	169(2)	N/A	22
8	(*p*-Tol)$_3$Sb(OOH)$_2$ · 2 THF						
	Sb (NILWIS)	2 OOH · S	O (THF)	2.736(2)	169(3)	N/A	22
			O (–$\underline{\text{O}}$OH)	2.703(3)	166(3)		
9	$Me_3Sb(OOH)_2$						
	Sb (NIMLAA)[b]	2 OOH	O (–$\underline{\text{O}}$OH)	2.773(6)	145.1	36.5	22
		n OOH	O (–$\underline{\text{O}}$OH)	2.782(5)	178(6)	35.4	
10	$Ph_3Sb(OOH)_2 \cdot 0.75\,THF$						
	Sb (NIMLEE)	3 OOH	O (–$\underline{\text{O}}$OH)	2.828(5)	157(5)	N/A	22
			O (–$\underline{\text{O}}$OH)	2.744(5)	152(5)		
			O (–O$\underline{\text{O}}$H)	2.798(7)	163(6)		
		3 OOH	O (–$\underline{\text{O}}$OH)	2.769(7)	169(5)		
			O (–O$\underline{\text{O}}$H)	2.775(7)	164(5)		
			O (–$\underline{\text{O}}$OH)	2.733(5)	166(5)		
11	Ph_3PbOOH						
	Pb (WEBPOM)	1 OOH · L	π (Ph)			13.7	4
d-block element hydroperoxo complexes							
15	$Lig_{Ph}Ni(OOH)$ (Lig_{Ph} = phenyl-substituted pincer ligand)						
	Ni (HOTREP)	1OOH · L	π (Ph)			20.5	32
16	$[Cu(bppa)(OOH)]ClO_4$ (bppa = bis(6-pivalamide-2-pyridylmethyl)(2-pyridylmethyl)amine)						
	Cu (NOBCIQ)	1OOH · L · S	O (ClO_4^-)	2.940(7)	147(7)	N/A	28
17	($^{Bu^t}$PCP)Pd(OOH) ($^{Bu^t}$PCP = [1,3-($CH_2PBu^t_2)_2C_6H_3]^-$)						
	Pd (RECKUG)	2 OOH	O (–$\underline{\text{O}}$OH)	2.696(4)	170(3)	N/A	26
18	$Tp^{Me_2}PtMe_2(OOH)$ (Tp^{Me_2} = hydrotris(3,5-dimethylpyrazolyl)borato)						
	Pt (GULKED)	2 OOH	O (–$\underline{\text{O}}$OH)	2.698(5)	139.5	N/A	27

[a] In case of atoms with disorder, the data on geometrical parameters of hydrogen bonds are presented considering the positions with the highest occupancy values. S = solvent molecule or anion. L = ligand other than a hydroperoxo one. The data on hydrogen bond energies E_{HB} (if available) are acquired from the quantum chemistry computations, see the corresponding references. [b] O_d and H atoms are disordered with 0.520(7)/0.480(7) occupancy ratio.

of hydroperoxo complexes as key intermediates in biological systems. The non-comprehensive list of transition metals and the so-based haem and non-haem enzymes proposed or found to contain hydroperoxo-coordinated species in their catalytic cycles includes Fe [cytochrome P450 (CYP), chloroperoxidase (CPO), horseradish peroxidase (HRP), haemerythrin (Hr) (Figure 5), isopenicillin-*N*-synthase (IPNS), myo-inositol oxygenase (MIOX), superoxide reductase (SOR), Rieske dioxygenases (RDOs)],[72–78] Cu [dopamine β-hydroxylase (DβH), peptidylglycine α-hydroxylating monooxygenase (PHM), lytic polysaccharide monooxygenases (LPMOs), galactose oxidase (GAO), copper–zinc superoxide dismutase (SOD-1), laccase],[79–83] Mn [manganese superoxide dismutase (MnSOD)],[84] and V [vanadium-dependent haloperoxidases (VHPOs)].[85] Accordingly, multitudinous biomimetic systems have been developed.[86,87] Curiously, local hydrogen bonding arrangement of the natural or artificial metalloenzyme active centre may adjust its reactivity. For example, oxyhaemoglobins require at least one hydrogen bond to the O_p atom to stabilize the Fe–O_2 species,[88] whereas the O–O bond cleavage in Fe^{III}–OOH complexes (known as Compound 0) is facilitated by the O_d atom protonation by surrounding amino acid residues or coordinated water, leading to the formation of highly electrophilic radical-cation $Fe^{IV}=O^{+\bullet}$ (Compound 1) or neutral $Fe^{V}=O(OH)$

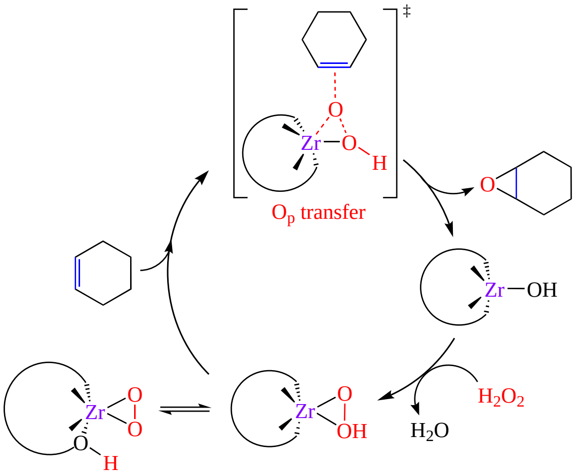


Figure 4 The exemplary proposed mechanism of cyclohexene epoxidation with H_2O_2 activated over Zr-monosubstituted Lindqvist tungstates involving Zr^{IV}–OOH as the active epoxidizing species.

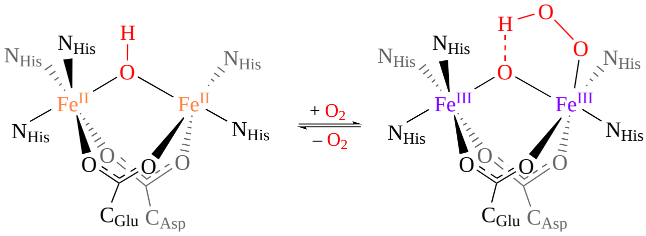


Figure 5 Dioxygen binding in the active site of haemerythrin resulting in the formation of Fe^{III}–OOH species.

species.[64,72] Analogously, Cu^{II}–OOH moieties are activated by a hydrogen bond to the O_d atom in DβH and LPMOs; this and the opposite case of stabilization by a hydrogen bond to the O_p atom was demonstrated for the mimicking systems.[61–63]

The chemistry of p-block element hydroperoxides has been the subject of many classic studies. Special attention was paid to decomposition mechanisms and transformations of organoelement hydroperoxo complexes (Si, Ge, Sn, Pb, Tl, Sb) into symmetrical or asymmetrical, mono- or bimetallic peroxides.[89–93] Nevertheless, so far there is little published data on application of isolated p-block element hydroperoxo complexes in catalytic oxidations of organic substrates, notwithstanding that theoretical results predict the involvement of such hydroperoxo-coordinated species.[94–98] Recently, two boron complexes bearing hydroperoxo ligands (no. 1 and no. 12 in Tables 1 and 3) were found to be reasonably stable mild oxidizing agents, transferring oxygen atom to triphenylphosphine.[37,38] Crystalline triphenyl Pb^{IV} monohydroperoxide and Sb^{V} dihydroperoxide (no. 11 and no. 10 in Tables 1 and 3) were probed as two-electron oxidants for olefin epoxidation mediated by chiral manganese complexes in the presence of carboxylic acid additives.[4,22,99] The proposed mechanistic pathways indicate the direct role of lead or antimony centre as the reactions proceed. Despite being somewhat inferior to aqueous hydrogen peroxide in terms of yield and enantioselectivity, these compounds overcome its noticeable disadvantages such as transition-metal-catalyzed disproportionation and synthetic protocol inconvenience. Even so, the toxicity and availability aspects suggest the significance of these findings for fundamental research rather than practical application.

Water-peroxide solutions of Sn^{IV} hydroxo compounds were first acknowledged as effective hydrogen peroxide stabilizers in the 1940s.[100] The equilibrium speciation in these systems has been studied in detail by ^{119}Sn NMR.[15,101] Upon increasing hydrogen peroxide concentration, the gradual replacement of hydroxo ligands by hydroperoxo ligands proceeds in the coordination sphere of tin in basic medium. The formed mixed hydroxo/hydroperoxo tin anionic complexes of different composition are observed in ^{119}Sn NMR spectra as separate resonance signals. For instance, stable crystalline hydroperoxostannates of alkali metals (Na, K, Rb, Cs) were isolated from highly concentrated (>90 wt%) hydrogen peroxide solutions and characterized with various physico-chemical techniques, including SCXRD (no. 4 and no. 14 in Tables 1 and 3).[39,40,102,103]

Hydroperoxo complexes of non-transition elements have received considerable attention as environmentally friendly and

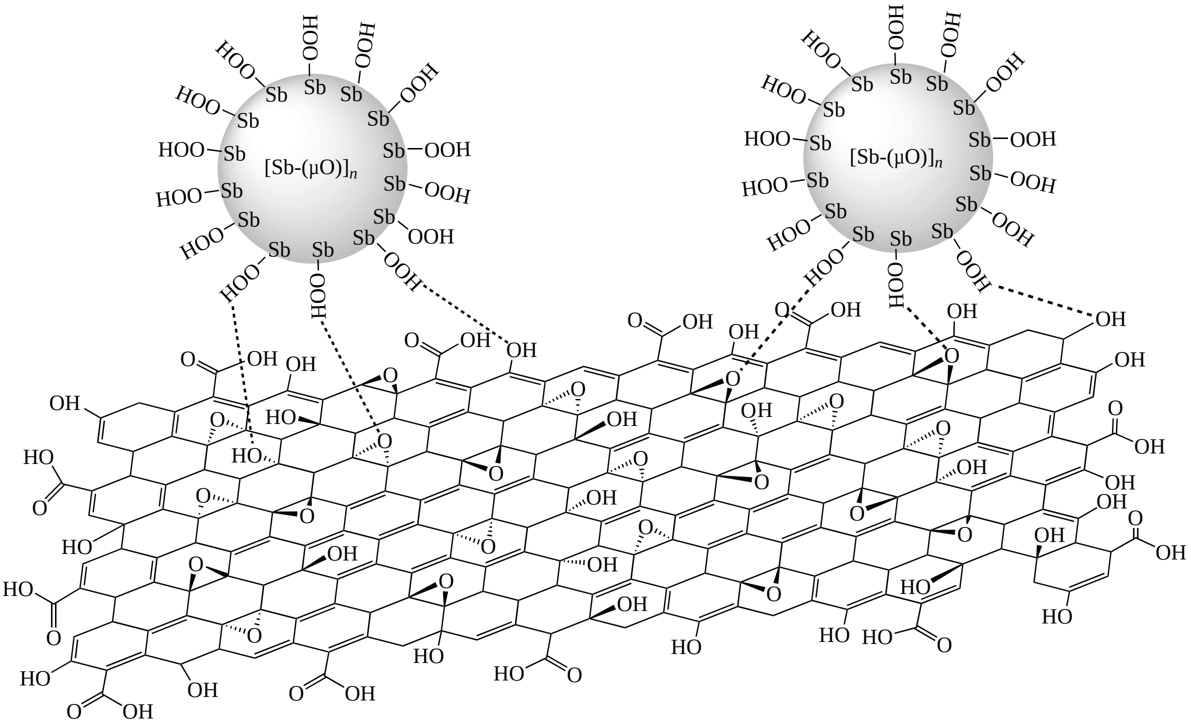


Figure 6 An illustration of hydrogen bonding interactions between terminal hydroperoxo ligands of peroxoantimonate-based sol particles and oxygen-containing functional groups on the surface of graphene oxide.

readily accessible functional material precursors. An apparently primary direction of their use concerns thin film coating technologies in accordance with the previously developed peroxide route.[104–106] The peroxide sol–gel process rests on utilizing hydrogen peroxide that under basic conditions converts the initial salts or hydroxides into (hydro-)peroxo complexes and serves as a capping agent, preventing them from further polycondensation.[15] The thin film formation on the surface of the support material, preliminary dispersed in the aqueous peroxide solution, is accomplished by an excess of an organic anti-solvent (ethanol, methanol, diethyl ether, or a mixture thereof), ensuring the quantitative precursor precipitation. It has been demonstrated that the presence of terminal hydroperoxo groups on the sol particle surface increases their affinity for the support material proton-acceptor sites, such as oxygen-containing functional groups on the surface of different clays or graphene oxide (Figure 6), and aromatic systems, as in graphene or reduced graphene oxide.[107,108] The corresponding O–H···O or O–H···π model hydrogen bonds were quantitatively described employing the periodic DFT computations.[4,109] Importantly, subsequent thermal and/or chemical (*e.g.* with hydrogen sulfide) treatment of the supported precursors makes it possible to obtain uniform nanoscale oxide or chalcogenide coatings of controllable composition. Particularly, new composite two-dimensional anode materials for lithium-, sodium-, and potassium-ion batteries have been prepared from inorganic sols based on (hydro-)peroxo-containing complexes of Sn, Sb, Te and Ge.[13,110–118] Likewise, functional materials of various morphology have been designed for gas sensing applications.[15,119]

The use of transition metal peroxo complexes in the preparation of oxide-based nanomaterials is well-known.[16,120,121] However, there are also mechanistic suggestions or direct observations with respect to the participation of less stable d-block element hydroperoxo species in material chemistry. By way of illustration, nanocrystalline zinc peroxide is believed to possess surface-allocated hydroperoxo ligands, explaining its activity towards the surfaces of muscovite and poly(melamine-formaldehyde) (Figure 7).[122,123] Moreover, a nickel cubane cluster with the alleged formation of bridging hydroperoxo groups (no. 28 in Table 2) was synthesized sonochemically from metal precursor and organic bidentate ligand in dilute methanol–water hydrogen peroxide solution and subjected to the open atmosphere thermolysis, yielding nanocrystalline nickel oxide in a rod shape.[55] Similarly, heating of barium trihydroxo(hydroperoxo)peroxostannate[14] (no. 13 in Table 1) provided barium stannate, applied in its lanthanum-doped form in an efficient and stable perovskite solar cell.[124] The absence of organic ligands in such peroxide-assisted approaches could account for the substantial decrease of crystallization temperature for target material, and synthesis sustainability, with oxygen and water being the sole by-products.

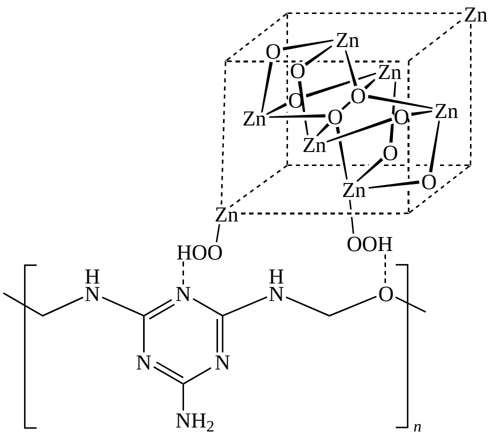


Figure 7 An illustration of hydrogen bonding interactions between terminal hydroperoxo ligands of zinc peroxide-based sol particles and triazine nitrogen and ethereal oxygen acceptors on the melamine–formaldehyde copolymer.

Conclusions

Ultimately, organoelement and inorganic hydroperoxo coordination compounds are of significant interest for various applications, including catalytic oxidation in organic synthesis, enzymatic and biomimetic studies, and material chemistry. This could be attributed to the generally high chemical activity of hydroperoxo complexes towards nucleophilic and/or electrophilic substrates, on the other side of the coin hampering their experimental description. Given sufficient thermal and moisture stability, these compounds can be isolated as crystalline solids and structurally characterized.

The CSD&ICSD analysis revealed geometrical parameters of hydroperoxo ligands for 13 and 11 reliable entries of p- and d-block element hydroperoxo complexes, respectively. The crystal structures of the former are substantially well-determined and hence might be utilized as model systems in research on catalytic dioxygen activation and proton-transfer reactions. By contrast, the latter repeatedly contain erroneous or ambiguous fragments, advising more careful structural and spectral studies to assure the correct assignment of the hydroperoxo moiety, in light of other possible dioxygen ligand forms. The following hydroperoxo coordination types were uncovered: η^1 (overall preferred), η^2, μ_2-η^1:η^1, μ_2-η^1:η^2, μ_2-η^2:η^2, μ_2-1κ*O*,2κ*O'*. The coordination fashions were concluded to be more diverse for transition metal complexes. The distances of hydrogen bonds donated by hydroperoxo ligands were found to be narrowly distributed and in average virtually coincide with crystalline peroxosolvates. Depending on the number of hydroperoxo and/or other ligands, solvent molecules and anions engaged in hydrogen bonding, several hydrogen-bonded motifs (HBMs) were discovered, from simple segregated fragments to infinite chains.

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