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Review

Peroxo complexes of niobium(V) and tantalum(V)

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Contents

Abstract

This review covers the literature about niobium(V) and tantalum(V) complexes containing at least one peroxo ligand in their coordination sphere. In addition to the synthesis aspects, the available structural data as well as several results issued from techniques like IR and Raman spectroscopies, NMR, thermal analyses or mass spectrometry are collected and discussed. This paper also includes a brief description of the applications of these compounds in catalysis and as precursors in materials science.

Keywords: Niobium; Tantalum; Peroxo complexes

Abbreviations: Cp, η^5-cyclopentadienyl; bpy, 2,2′-bipyridine; dme, dimethoxyethane; gu, guanidinium; Hacac, acetylacetone; Hdbm, dibenzoylmethane; Hbtfa, benzoyltrifluoroacetylacetone; Httfa, thenoyltrifluoroacetylacetone; Hhfa, hexafluoroacetylacetone; H_2ox, oxalic acid; H_4tart, tartaric acid; H_4cit, citric acid; H_2glyc, glycolic acid; H_3mal, malic acid; H_4edta, ethylenediaminetetraacetic acid; H_4pdta, propylenediaminetetraacetic aci; H_5dtpa, diethylenetriaminepentaacetic acid; H_6ttha, triethylenetetraaminehexaacetic acid; Hpic, picolinic acid; HpicO, picolinic acid *N*-oxide; H_2dipic, dipicolinic acid; Hhq, 8-hydroquinoline; H_2pzdc, pyrazine 2,5-dicarboxylic acid; H_2salen, bis(salicylaldehyde) ethylenediamine; H_2hnpren, bis(2-hydroxy-1-naphthaldehyde) propylenediamine; H_2haed, bis(2-hydroxy acetophenone)ethylenediamine; H_2hned, bis(2-hydroxy-1-naphthaldehyde)ethylenediamine; H_2acen, bis(acetylacetonate) ethylenediamine; H_2salphen, bis(salicylaldehyde) phenylenediamine; H_2anac, acetylacetonatebis(anthranilic acid); H_2salpren, bis(salicylaldehyde) propylenediamine; H_2sac, salicylaldehyde anthranilic acid; H_2sap, salicylaldehyde *o*-aminophenol; H_2hntrien, bis(2-hydroxy-1-naphthaldehyde)1,2-aminopropane; H_2hphpd, 3(2-hydroxy)phenylhydrazono pentane 2,4-dione; PAC, polyaminocarboxylate; phen, 1,10-phenantroline; TPP, tetraphenylporphyrin

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1. Introduction

The interest for the two heaviest elements of group 5, niobium and tantalum, is essentially related to the multiple uses of these elements in advanced materials for high technology applications: this is first the case in the metallurgical field, where Nb is involved in the production of several stainless steels that can be used at elevated temperatures, and for Ta because of its extreme resistance to corrosion at normal temperature. Because Ta is currently thought to be inert to body fluids, it appears as an ideal material for surgical uses in bone repair and internal suturing. Ta is also widely used in electronics, for the manufacture of capacitors because it readily covers with an oxide film that acts as an efficient insulator. Other fields of application are catalysis (both homogeneous and heterogeneous), ferroelectrics and superconductors.

However, the aqueous chemistry of these two elements is known to be quite restricted. Both metals are actually very resistant to acids but can be dissolved in HNO_3-HF mixtures, and display very little cationic behaviour. While Nb also displays the oxidation state +IV, Ta is exclusively present in its +V state, with very few water-soluble compounds. A combined study of these two elements is justified by the fact that Nb(V) and Ta(V) compounds often exhibit very pronounced chemical and structural similarities. This is the consequence of virtually identical ionic sizes of 4d and 5d ions as a result of the so-called "lanthanide contraction". A further immediate consequence is that the criteria for obtaining heterometallic Nb–Ta structures are in principle fulfilled when isostructural compounds are known for both elements.

Research on the coordination chemistry of Nb and Ta has helped a lot to develop new methods aiming at incorporating these elements in specific materials, or to improve the existing ones. More particularly, peroxide compounds of niobium and tantalum, as well as of vanadium, have attracted considerable attention in the last decades. These compounds show the ability to release oxygen in active form, either chemically or on irradiation, and act in oxidations of different inorganic and organic substrates like sulfides, sulfur dioxide, alkenes, alcohols, aromatic and aliphatic hydrocarbons and phosphines [1–12]. These processes, either stoichiometric or catalytic, use hydrogen peroxide or alkylhydroperoxides as oxidant, are usually carried out in mild conditions and are associated to good yield and selectivity. Moreover, in the case of vanadium, the growing interest for peroxide species results from the important role it plays in biological systems. For example, peroxide vanadium(V) complexes have been found to have anti-tumour and insulin mimetic activities, while other have been studied as functional models for the vanadium haloperoxidase enzymes [13–15]. Finally, because such peroxide-type coordination compounds of group 5 elements are most of the time soluble, in water or in other organic solvents, they are also of great interest as precursors for the preparation of oxide materials and more particularly, multimetallic oxides, via a wet-chemical solution route [16–26]. The main advantages of such a "precursors method" are the formation of crystalline and homogeneous materials under conditions significantly milder than those employed in conventional solid state synthesis like the ceramic method. This application of peroxide complexes of group 5 elements has been particularly developed in the literature during the last years because of the attractive properties of vanadium and niobium-containing oxides. For example, such materials are widely studied as ferroelectrics [17,27], as ions conductors [28] or as catalysts in several highly challenging industrial processes, like alkane oxidation [29–32] or ammoxidation [33,34] and water photodecomposition [35,36].

On the one hand, the chemistry of peroxides compounds of vanadium was already thoroughly reviewed by Butler et al. [37] in 1994 and more recently by Bortolini and Conte [38]. On the other hand, there has been no subsequent review that has focused on complexes of niobium and tantalum with peroxide ligands. For this reason, the present review covers all compounds of these last two elements that incorporate at least one O_2^{2-} ligand and have been characterized in the solid state. Numerous polyoxometallates based essentially on tungsten and/or silicon and containing peroxide-niobium or tantalum unit(s) have been described in the last few years in the context of catalytic oxidations or epoxidations of organic substrates or even as potential anti-HIV agents [39–43]. These compounds will not be under the focus of this review.

Peroxide complexes of transition metals are generally classified according to the bonding mode of the peroxide group. In the case of a non-bridging O_2^{2-} ligand, η^1 "superoxo", η^1 "hydroperoxo", and η^2 "peroxo" examples are known. Bridging peroxide can adopt η^1:η^1 (M–O–O–M), η^2:η^2, η^1:η^2 or even η^3:η^3 configurations. In the particular case of Nb and Ta, all the peroxide complexes described in the literature contain one or more O_2^{2-} ligand(s) bound in a η^2 coordination mode, and are referred to as "peroxo compounds".

In this review, the discussion is organized according to the type of peroxo compounds based on the co-ligand(s) present in the coordination sphere. Section 5 is dedicated to the different applications of the peroxo species of niobium(V) and tantalum(V). In the following discussion, the letter M used in formula refers to niobium as well as to tantalum.

2. Homoleptic peroxo complexes

In the beginning of the 20th century, Balke noticed, while testing niobium or tantalum hydroxide, also called niobic and tantalic acid, respectively, that they dissolved in an alkaline solution of hydrogen peroxide [44,45]. The species then formed in solution is the corresponding complex with the highest possible content of peroxo groups, the tetraperoxometallate anion $[M(O_2)_4]^{3-}$. A wide range of such tetraperoxometallate compounds have been reported because of the diversity of counterions used to obtain the salt. They have been prepared with alkaline cations like sodium, potassium, rubidium and cesium, and also with ammonium and guanidinium ions ($CN_3H_6^+$, noted gu^+). Some double salts have also been described. Table 1 lists all the tetraperoxoniobates and -tantalates reported so far in the literature.

Several preparation methods of $C_3^I[M(O_2)_4]\cdot nH_2O$ have been described and all consider the reaction of a niobium or tantalum precursor with H_2O_2 in excess and a source of the counter-

Table 1
Tetraperoxoniobate and -tantalate complexes described in the literature

Tetraperoxoniobate	Reference
$Na_3[Nb(O_2)_4]$	[45]
$Na_3[Nb(O_2)_4]\cdot 13H_2O$*	[3]
$NaMg[Nb(O_2)_4]$	[45]
$NaCa[Nb(O_2)_4]$	[45]
$K_3[Nb(O_2)_4]$	[45,51,54,57,58,64]
$K_3[Nb(O_2)_4]\cdot 1/2H_2O$	[52]
$KMg[Nb(O_2)_4]\cdot 7H_2O$*	[45,65]
$KCa[Nb(O_2)_4]\cdot 4H_2O$	[45]
$Rb_3[Nb(O_2)_4]$*	[45,51,53,64]
$RbMg[Nb(O_2)_4]\cdot 7/2H_2O$	[45]
$Cs_3[Nb(O_2)_4]$	[45,51,64]
$CsMg[Nb(O_2)_4]\cdot 8H_2O$	[45]
$Cs_2NH_4[Nb(O_2)_4]$	[51]
$(NH_4)_3[Nb(O_2)_4]$	[16,50,51,55,56,64]
$(gu)_3[Nb(O_2)_4]$*	[16,51]
$Na_3[Ta(O_2)_4]$	[44]
$Na_3[Ta(O_2)_4]\cdot H_2O$	[46]
$K_3[Ta(O_2)_4]$*	[44,46,47,49,54,57,58]
$K_3[Ta(O_2)_4]\cdot 1/2H_2O$	[46,46,52]
$KCa[Ta(O_2)_4]\cdot 2H_2O$	[44]
$KCa[Ta(O_2)_4]\cdot 9/2H_2O$	[46]
$Rb_3[Ta(O_2)_4]$*	[49]
$Cs_3[Ta(O_2)_4]$	[49]
$KMg[Ta(O_2)_4]\cdot 2H_2O$	[44]
$(NH_4)_3[Ta(O_2)_4]$	[49,50,55,56]
$(gu)_3[Ta(O_2)_4]$*	[48]

* Crystal structures have been solved.

cations. In all cases, the solid compound has been isolated from the clear aqueous solution by adding acetone or ethanol. Balke first described the preparation of $[Ta(O_2)_4]^{3-}$ from the tantalum hydroxide, H_2O_2 and sodium or potassium hydroxide [44]. They also reported the preparation of $C_3^I[Nb(O_2)_4]\cdot nH_2O$ complexes (C^I = Na, K, Rb, Cs) by adding H_2O_2 in excess to a solution containing the corresponding alkaline niobate and an excess of the proper alkali carbonate or hydroxide [45]. Double salts were prepared by double decomposition of an alkaline tetraperoxoniobate or -tantalate with the alkaline-earth chloride, $CaCl_2$ or $MgCl_2$ [44–46]. More recently, three major modes of synthesis of tetraperoxometallate complexes of niobium or tantalum have been used: (i) the dissolution of the niobic or tantalic acid, often obtained from hydrolysis of the corresponding pentachloride in basic medium, in a concentrated H_2O_2 solution and in the presence of KOH [47], NH_3 or gu_2CO_3 [16,48]; (ii) the reaction of MCl_5 with H_2O_2 and NH_3 or gu_2CO_3 [49–51]; and finally, (iii) the fusing of the metal pentoxide, M_2O_5 with the alkaline hydroxide (Na, K) [3,46,52] or carbonate (K, Rb, Cs) [49,53] followed by the dissolution of the melt with a solution of H_2O_2.

Semiquantitative measurements of solubility have been carried out by Shchelokov et al. on several niobium complexes [51]. Their solubility in aqueous solution ranges from 0.03 to 1 g ml^{-1} and decreases along the sequence Cs^+, Rb^+, $Cs_2NH_4^{3+}$, K^+, gu^+, NH_4^+, from the stronger to the weaker base [51].

The thermal behaviour of such tetraperoxometallates of niobium and tantalum has also been widely examined by thermal analyses (TGA, SDTA and DSC) [16,48,50,51,54–56]. Most of them show a poor thermal stability. They decompose with a marked exothermic effect, observed by SDTA or DSC methods, in the corresponding orthometallate, $C_3^IMO_4$ ($C^I = Na^+$, K^+, Rb^+, Cs^+) [51] or the pentoxide, M_2O_5 in the case of the ammonium and guanidinium derivatives [16,48,56]. Decomposition schemes have been proposed for the ammonium and potassium compounds [50,54,55] and the kinetics of solid state degradation of $K_3[Nb(O_2)_4]$ and $K_3[Ta(O_2)_4]$ have also been studied in detailed under isothermal and dynamic conditions [54,57]. Some tetraperoxo compounds like the cesium-ammonium, the ammonium and the guanidinium derivatives of niobium give rise to a violent decomposition on heating with considerable evolution of gas and dispersion of the residue, similar to an explosion [16,50,51,55]. The energetic characteristics of the explosive behaviour of the $(NH_4)_3[M(O_2)_4]$ complexes have even been discussed [55].

Infrared and Raman spectra of tetraperoxometallate compounds display characteristically bands occurring from the presence of the side-bonded peroxo ligands. Two types of vibrational modes are expected: the peroxo stretching, ν(O–O) and the metal-peroxo stretching, $\nu[M(O_2)]$. These vibration modes are insensitive to the nature of the metal. One broad or two ν(O–O) bands are observed in IR and two such bands in Raman, near 810 cm^{-1} [16,49–52,58,59]. As far as the metal-peroxo stretching vibrations are concerned, two modes occur in the spectra: the first one, $\nu_{as}[M(O_2)]$ is observed in both techniques while the second one, $\nu_s[M(O_2)]$ is present only in Raman. These bands are observed near 550 and 530 cm^{-1}, respectively [16,59,60]. Two recent studies have been reported on the vibrational spectra of tetraperoxometallate compounds. In the first one, the authors determined, for $(C^I)_3[Ta(O_2)_4]$ ($C^I = K^+$, Rb^+, Cs^+), the different vibrational modes of the O–O and Ta–O stretching vibrations from the site group analysis of the $[Ta(O_2)_4]^{3-}$ anion (site group symmetry D_{2d}) [49]. The second one deals with the theoretical simulations of experimental observations made by IR and Raman spectroscopies on peroxo complexes of Nb(V) and Ta(V). The calculations have been performed at DFT level using various functionals and provided the normal modes of vibrations involving peroxo ligands, their corresponding frequency and their activity in IR and/or Raman spectroscopy [60].

Other theoretical studies have been carried out on tetraperoxometallate species concerning their molecular electrostatic potential and their electronic deformation densities [61,62]. Multiple scattering-Xα molecular orbital calculations are reported for the $[Nb(V)(O_2)_4]^{3-}$, $[Cr(V)(O_2)_4]^{3-}$ and $[Mo(VI)(O_2)_4]^{2-}$ anions. The bonding is discussed in terms of the interaction between the metal ion and the peroxide fragments.

Several papers describe powder X-ray diffraction of Nb and Ta tetraperoxo complexes. The XRD patterns of $K_3[M(O_2)_4]$, $Rb_3[M(O_2)_4]$, $Cs_3[M(O_2)_4]$, $(NH_4)_3[M(O_2)_4]$ indicate that they are isostructural and crystallize in the $K_3[Cr(O_2)_4]$-type [49,50,63,64]. In all cases, the X-ray powder data could be fully indexed on the basis of the tetragonal system and the lattice parameters could be determined by calculations.

The crystal structures of $Na_3[Nb(O_2)_4]\cdot 13H_2O$, [3] $KMg[Nb(O_2)_4]\cdot 7H_2O$, [65] $Rb_3[Nb(O_2)_4]$ [53], $gu_3[Nb(O_2)_4]$ [16], $K_3[Ta(O_2)_4]$ [47], $Rb_3[Ta(O_2)_4]$ [49] and $(gu)_3[Ta(O_2)_4]$

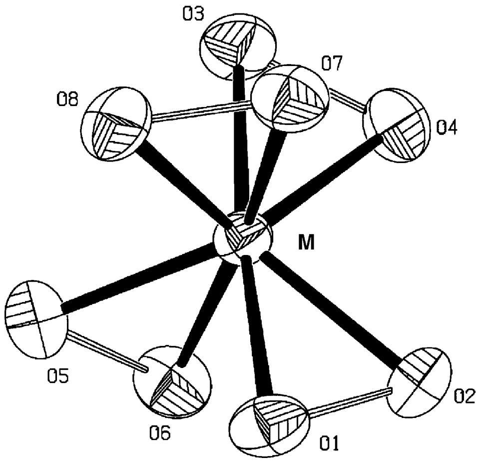


Fig. 1. Structure of $[M(O_2)_4]^{3-}$.

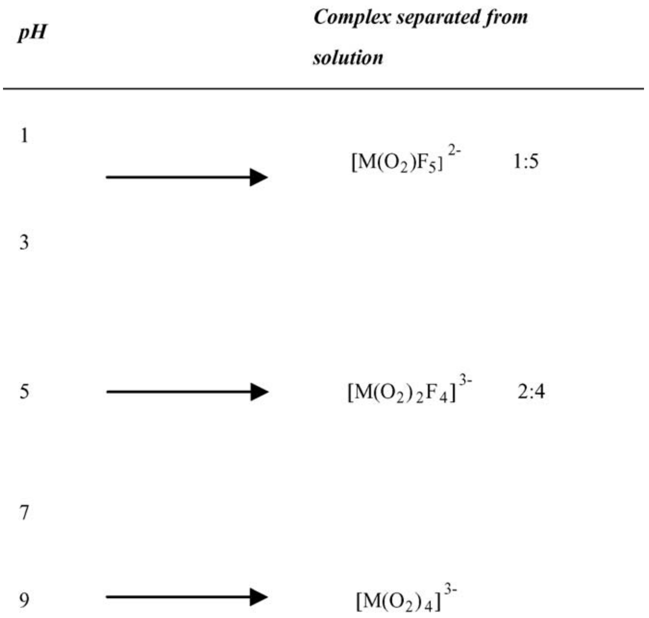
[48] have been determined and reveal the $[M(O_2)_4]^{3-}$ anion to possess a dodecahedral geometry (D_{2d}), on the basis of a tetrahedral arrangement of four η^2–$O_2{}^{2-}$ ligands around the metal atom, which thus presents an eight-fold coordination (Fig. 1). There are no significant differences in the metal-oxygen bond lengths for the different niobates and tantalates described. These distances range from 1.993 to 2.066 Å and the O–O bond length ranges from 1.491 to 1.509 Å [16,47–49,53,65]. But, according to some authors, the distances between the metal and the two oxygen atoms of a peroxo group are not equal, but only slightly different [47,49,53].

3. Heteroleptic peroxo complexes

3.1. Heteroleptic peroxo complexes containing halide co-ligands

The great majority of halide-containing peroxo compounds of niobium and tantalum described in the literature correspond to fluoro species. Some complexes with chloro ligands in their coordination sphere are also reported but in a less extended way.

In the aqueous solutions of niobates and tantalates containing excess hydrogen peroxide and hydrofluoric acid, peroxo–fluoro complexes are present. They can be separated from the solutions, the peroxo/fluoro ratio in the isolated salts depending drastically on the pH [66]. At low pH, one peroxo group enters the coordination sphere and 1:5 monoperoxopentafluoro niobate or tantalate can be obtained. On raising the pH in the range 4–6, one further peroxo ligand is incorporated in the complex to yield 2:4 diperoxotetrafluoro species. On further increasing the pH, all the fluoro ligands are substituted by peroxo groups, and the well-known tetraperoxometallate complex is obtained. Indeed, the process is reversible. By dissolving the tetraperoxo species, adding fluoride ions and decreasing the pH, diperoxotetrafluoro complexes can be prepared. The exchange of fluoro ligands by peroxo groups on increasing the pH is illustrated in Scheme 1 [66]. From an experimental point of view, peroxo–fluoro complexes are mainly prepared from the pentoxide, M_2O_5 dissolved in concentrated HF and H_2O_2 in excess, in the presence of a source of the counter-ion. pH is sometimes adjusted depending on the peroxo/fluoro stoichiometry desired: 1:5, $(C^I)_2[M(O_2)F_5]$ ($C^I = Na^+$, K^+, Rb^+, Cs^+, $NH_4{}^+$, 8-hydroxyquinolinium, *o*-phenantrolinium) or 2:4, $(C^I)_3[M(O_2)_2F_4]$ ($C^I = Na^+$, K^+, $NH_4{}^+$) [45,66–77]. 1:5 and 2:4 peroxo–fluoro species with potassium counter-ions have also been obtained electrochemically from a Nb or Ta metallic anode [78]. 1:4 aqua-peroxo–fluoro species, $(Et_4N)[M(O_2)F_4(H_2O)]$ (M = Nb or Ta) have also been obtained [79,80]. Finally, 1:5 monoperoxopentachloro complexes have been prepared from the tetraperoxometallate in concentrated HCl medium followed by saturation of the solution by gaseous HCl [81]. Some tantalum compounds have also been synthesized from $TaCl_5$ and the counter-ion chloride (NH_4Cl, RbCl or CsCl) in HCl/H_2O_2 medium saturated by gaseous HCl [82]. Peroxo-halogeno compounds with organic ligands, $(Et_4N)[M(O_2)F_3(L)]$ [79,80], $(Et_4N)[Nb(O_2)Cl_3(L)]$ [83] and $(Et_4N)[Ta(O_2)F_4(L')]$ [84] with HL = Hacac, HdbmH, Hbtfa, Httfa, Hhfa and L′ = 2-methylpyridine *N*-oxide, have been obtained from the corresponding aqua-monoperoxotetrahalogeno species, $(Et_4N)[M(O_2)X_4(H_2O)]$ (X = Cl or F), by substituting in the coordination sphere the water molecule and one halide by the organic ligand, L or L′. $[M(O_2)F_3(L)]$ complexes (L = phen or triphenylarsine oxide) [85] as well as dimeric species with oxalate, $(Et_4N)_2[Nb_2(O_2)_2F_6(ox)]$ [79] and 2,2′-bipyridine, $[M_2O(O_2)_2F_4(bpy)_2]$ [85] have also been prepared according the same way. Finally, $[M(O_2)_2Cl(L)]$ (L = pyridine *N*-oxide, 2-aminopyridine, triphenylphosphine oxide, triphenylarsine oxide) have been recently synthesized by Tarafder et al. from the pentachloride in the presence of H_2O_2 and the ligand [5,6].



Scheme 1. pH-dependence of the substitution of fluoro ligands by peroxo groups in niobate and tantalate complexes [66].

Peroxo-halogeno species are in general stable in ambient air at room temperature and no particular precaution is required to store or handle them under inert atmosphere. The peroxo-halogeno species which do not contain organic ligands are soluble in water as well as in some classical organic solvents while those with such ligands are soluble only in organic medium.

Thermal analyses in the solid state have been carried out on peroxo–fluoro species of niobium and tantalum. Kinetics of decomposition of $K_2[M(O_2)F_5]\cdot H_2O$ and $K_2[M(O_2)_2F_4]$ under isothermal conditions have been studied [54,70,71,86]. The same study has been carried out in dynamic conditions for the $K_2[Nb(O_2)_2F_4]$ complex [54]. The reaction scheme of thermal decomposition has been determined and is represented by the Eqs. (1) and (2).

$$K_2[M(O_2)F_5]\cdot H_2O(s) \rightarrow K_2MOF_5(s) + 1/2O_2(g) + H_2O(g) \qquad (1)$$

$$K_3[M(O_2)_2F_4](s) \rightarrow K_3MO_2F_4(s) + O_2(g) \qquad (2)$$

Both processes are described as exothermic, irreversible and yield the corresponding solid oxofluorometallate. The kinetics of photodecomposition has also been investigated for the tantalum derivatives, $K_2[Ta(O_2)F_5]\cdot H_2O$ and $K_2[Ta(O_2)_2F_4]$ [71,87].

For a number of peroxo–fluoro complexes of niobium and tantalum, some structural informations have been obtained from several techniques like vibrational spectroscopies [5,6,66,67,78–80,85,88–92] and ^{19}F NMR [79,80,83,88,93]. These peroxo–fluoro species display a pentagonal bipyramidal arrangement around the metal atom, which is consistent with a seven-fold coordination. Only one example of a six-fold coordination of Nb(V) and Ta(V) is given by Tarafder et al. for the $[M(O_2)_2LCl]$ complexes with a monodentate ligand (L = pyridine *N*-oxide, triphenylphosphine or triphenylarsine), but no structural investigation has confirmed this assumption.

The common features of the IR and Raman spectra of the peroxo–fluoro complexes in general are the vibrational modes due to the side-bonded peroxo ligand(s), viz. ν(O–O), $\nu_{as}[M(O_2)]$ and $\nu_s[M(O_2)]$, which appear in the regions 900–800 and 670–500 cm^{-1}, respectively. Other common features in the spectra are the metal-fluorine stretching modes which appear as several strong bands around 500 cm^{-1}, and which may also be overlapped by the symmetric $[M(O_2)]$ vibration [5,6,66,67,78–80,85,88–92]. The $[M(O_2)F_5]^{2-}$ ion has been studied in details by vibrational spectroscopies. Assignments of the different fundamental vibration modes related to the metal-peroxo unit, as well as those associated with the niobium-fluorine bonds, have been determined by normal coordinate calculations, on the basis of a C_{2v} symmetry [90,91]. Moreover, in the case of the dimeric species described with the oxalate and bipyridine ligands, IR spectroscopy was of great help to determine the coordination of the ligand and the complex structure. In the $(Et_4N)_2[Nb_2(O_2)_2F_6(ox)]$ complex, the oxalate ligand is bridging the two metal atoms in a tetradentate mode and the local symmetry is close to D_{2h} [79]. Comparison has been carried out with bands observed on the IR spectrum of $Na_3[NbO(ox)_3]\cdot H_2O$, in which the oxalate ligands are each bidentate (C_{2v} symmetry) [94]. In the IR spectra of $[M_2O(O_2)_2F_4(dpy)_2]$, an intense and broad band appearing at 800 and 830 cm^{-1} for the niobium and tantalum derivative, respectively, is assigned to the M–O–M bridge [85]. The authors have reported a molecular structure for the niobium complex. Both monomeric units are connected by an oxygen atom (Nb–O–Nb angle ~170°) and the coordination geometry is described as two pentagonal bipyramids connected by one of their apices, as illustrated in Fig. 2 [85]. In addition, IR spectra have also been interpreted in details for peroxo-chloro compounds, $[M(O_2)Cl_5]^{2-}$ [82,95]. The number as well as the symmetry of the vibration modes have been determined by Wendling on the basis of the Group Theory and compared with experimental results [95].

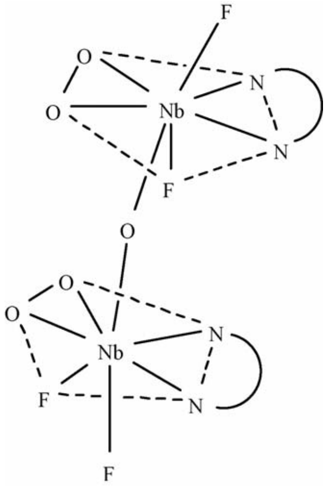


Fig. 2. Coordination geometry in the dimeric species $[Nb_2O(O_2)_2F_4(dpy)_2]$ [85].

As previously mentioned, ^{19}F NMR is a valuable tool for the study of fluoro compounds in general. This technique was first used by Evans et al. for the study of monoperoxopentafluoro compound of tantalum, $[Ta(O_2)Cl_5]^{2-}$ [88].The spectra of an aqueous solution of the potassium salt display a doublet and a quintuplet of relative intensities 4:1. This pattern shows the presence in the complex of four equivalent and one non-equivalent fluorine atoms, which means that the geometry around the tantalum atom possesses the C_{2v} structure, four F atoms in a square plane, one F atom and the peroxo group in the apical positions [88]. The five F atoms form in that way a square pyramid. The ^{19}F NMR analysis of the $[M(O_2)F_4(H_2O)]^-$ anion gives rise to one single signal which proves that the four fluorine atoms are equivalent and the structure is in agreement with that proposed by Evans et al. for $[Ta(O_2)Cl_5]^{2-}$ [88]: the fluorine atom in the apical position of the bipyramid is replaced by one water molecule in the first one [79]. The chemical environment of the metal has also been determined by ^{1}H and ^{19}F NMR for the series of compounds with β-diketonato ligands, $(Et_4N)[M(O_2)F_3(L)]$ (L = acac, dbm, btfa, ttfa, hfa) [79,80] while the influence of the oxo and peroxo ligands on the stereolability of chelated hexa- and heptacoordinated chloro species of Nb has been studied by ^{1}H NMR [83]. The oxo complex $[NbOCl_3(L)]^-$ (L = acac, dbm, btfa, ttfa, hfa) displays an octahedral geometry with a terminal Nb=O bond. Ligand exchange phenomena take place in this anion and seem to proceed via an intramolecular Ray-Dutt or Bailar mechanism, resulting in modification of the *cis–trans* stereochemistry. By incorporating a bidentate peroxo group in the coordination sphere, the resulting heptacoordinated species, $[Nb(O_2)Cl_3(L)]^-$ lose their potential stereolability, and the motions occurring in the corresponding oxo complex become impossible. The rigidity of the peroxo compound is due, according to the authors, to the bidentate nature of the $O_2{}^{2-}$ ligand which rules out some twisting mechanisms [83].

EPR analyses have been carried out by Geetha et al. on a γ-irradiated single crystal of the diperoxopentafluoroniobate, $K_2[Nb(O_2)F_5]\cdot H_2O$ as well as on the Mo-doped derivative [68,69].

The same authors have also described the crystal structure of the monohydrate potassium salt of the monoperoxopentafluoro complex of niobium, $K_2[Nb(O_2)F_5]\cdot H_2O$ [69]. In the $[Nb(O_2)F_5]^{2-}$ anion, the metal atom is heptacoordinated. The possible geometries for seven-coordination are the monocapped octahedron, the monocapped trigonal prism and the pentagonal bipyramid. The interatomic distances play an important role in deciding the geometry favoured in the complex. Three F atoms and one O atom from the peroxo group form a square equatorial plane, while the second oxygen atom from the peroxo is out-of-plane. The coordination geometry is thus described by the authors as a monocapped octahedron. This result is in contradiction with conclusions from Stomberg who has solved the structure of similar 1:5 niobium complexes with different counter-ions, $Na_2[Nb(O_2)F_5]\cdot H_2O$ [96], $Na_2[Nb(O_2)F_5]\cdot 2H_2O$ [73], $Na_3[HF_2][Nb(O_2)F_5]$ [72] and $(C_{12}H_{10}N_2)[Nb(O_2)F_5]$ [75]. The structures of $(C_9H_8NO)_2[Nb(O_2)F_5]\cdot 3H_2O$ and $K_3[HF_2][Ta(O_2)F_5]\cdot H_2O$ had been previously determined by Ruzic-Toros et al. [97,98] using the film method, but were reinvestigated and refined by Stomberg [74,76]. In those six monoperoxopentafluoro compounds, the metal atom always exhibits a seven-fold coordination but in each case, the polyhedron is described by the authors as a pentagonal bipyramid and the symmetry of the anion is almost C_{2v}. The peroxo group and three fluorine atoms form the equatorial plane while the two remaining fluorine atoms occupy the apices. Crystal structure determinations have also been made for 2:4 diperoxotetrafluoro species of stoichiometry $K_3[M(O_2)_2F_4]$ and $(NH_4)_3[M(O_2)_2F_4]$ [99]. The ammonium or potassium salts of niobium and tantalum are isostructural. In these complexes, the metal is surrounded by eight atoms and in the case of the ammonium derivatives, the coordination polyhedron, illustrated in Fig. 3, is described as an octahedron with two corners at the centre of the peroxo bond and the four fluorine atoms in the equatorial plane [99]. Schmidt et al. have observed a high disorder of the peroxo groups in the structure of the anion $[Ta(O_2)_2F_4]^{3-}$ solved in the case of the ammonium salt [92]. The structure of a tantalum complex containing a μ-oxo unit has also been described structurally. The compound of stoichiometry $K_6[Ta_3(O_2)_3OF_{13}].H_2O$ displays in its network monoperoxopentafluoro anions, $[Ta(O_2)F_5]^{2-}$ together with μ-oxo-diperoxo-octafluoro-ditantalate anions, $[Ta_2O(O_2)_2F_8]^{4-}$ [100].The arrangement of the ligands around the $[Ta(O_2)F_5]^{2-}$ species is identical to that already described in $K_3[HF_2][Ta(O_2)F_5]\cdot H_2O$ [74] while the coordination geometry of the dimeric $[Ta_2O(O_2)_2F_8]^{4-}$ anion, illustrated in Fig. 4, can be described as two corner-sharing octahedra, each one with one corner at the centre of the peroxo bond, three fluorine atoms and the oxygen from the μ-oxo group in the equatorial plane, the remaining F atom being in an apical position. Both octahedra are centrosymmetrical [100]. The structure of a peroxo–fluoro tantalum compound, $(Et_4N)[Ta(O_2)F_4(L)]$ with the organic co-ligand 2-methylpyridine *N*-oxide has been solved [84]: in the complexed anion, the tantalum atom is surrounded by one monodentate pyridine *N*-oxide ligand, four fluorine atoms and one peroxo groups. The seven-fold coordinated metal lies at the centre of a pentagonal bipyramid, the equatorial plane of which comprising the peroxo group, two fluorine atoms, and the oxygen from the *N*-oxide group of the organic ligand which is opposite to the bidentate ligand. The two capping positions are occupied by the two remaining fluorine atoms [84]. Table 2 lists, for most of the resolved structures of peroxo–fluoro compounds, the reported values of M–F, M–O and O–O coordination distances.

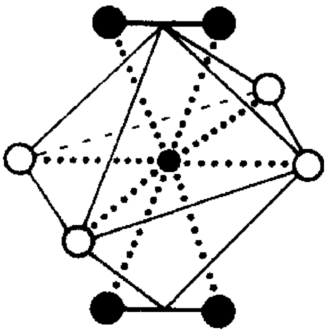


Fig. 3. Structure of the $[M(O_2)_2F_4]^{2-}$ anion showing the pseudo-octahedral geometry. The fluorine atoms are represented by open circles while oxygen atoms by black circles. Reproduced from Ref. [99], with permission from copyright owners.

No single crystal structure determination of peroxo-chloro complexes of Nb or Ta has been reported so far. However, some powder XRD analyses have been carried out on 1:5 species. The $(C^I)_2[M(O_2)Cl_5]$ compounds with $C^I = K^+, NH_4{}^+, Rb^+$ and Cs^+ are isostructural and crystallize in the cubic system [81,82,101]. Their reticular parameter *a*, in the range 9.90–10.25 Å, is not significantly different between the niobium and tantalum derivatives, in accordance with the close ionic radii of these ele-

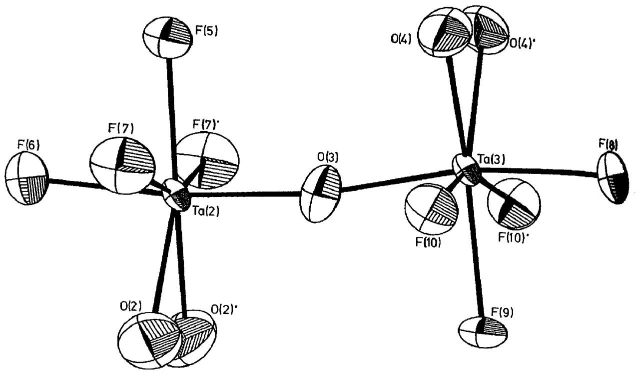


Fig. 4. Structure of the dimeric μ-oxo-diperoxo-octafluoro-ditantalate(V) anion, $[Ta_2O(O_2)_2F_8]^{4-}$ observed in the $K_6[Ta_3(O_2)_3OF_{13}]\cdot H_2O$ compound. Reproduced from Ref. [100], with permission from copyright owners.

Table 2
M–F, M–O and O–O bond lengths (in Å) for the peroxo–fluoro niobates and -tantalates described structurally

	M–F (Å)	M–O (Å)	O–O (Å)	Reference
$Na_2[Nb(O_2)F_5]\cdot H_2O$	1.938(4) 2.037(4) 1.906(4) 1.976(4)	1.928(4)	1.476(7)	[96]
$Na_2[Nb(O_2)F_5]\cdot 2H_2O$	1.936(4) 1.987(7) 1.938(4)	1.933(12) 1.962(14)	1.506(26) 1.411(31)	[73]
$Na_3[HF_2][Nb(O_2)F_5]$	1.988(2) 1.975(2) 1.906(2) 1.936(2) 2.019(2)	1.940(2) 1.924(2)	1.481(4)	[72]
$(C_{12}H_{10}N_2)[Nb(O_2)F_5]$	1.962(4), 1.980(4) 1.971(6), 1.958(6) 2.127(3), 1.913(2) 1.963(6), 1.931(2)	1.884(5) 1.924(10) 1.872(6) 1.883(8)	1.483(8) 1.440(16)	[75]
$(C_9H_8NO)_2[Nb(O_2)F_5]\cdot 3H_2O$	1.983(4) [170 K], 1.97(1) [275 K] 1.906(6) [170 K], 1.89(1) [275 K] 1.941(6) [170 K], 1.92(1) [275 K] 1.892(10) [170 K], 1.91(1) [275 K] 2.008(5) [170 K] 1.98(1) [275 K] 1.900(6) [170 K], 1.89(1) [275 K]	1.967(14) [170 K], 1.89(1) [275 K] 1.956(13) [170 K], 2.00(2) [275 K] 2.015(10) [170 K], 1.99(2) [275 K] 1.872(14) [170 K], 1.83(3) [275 K]	1.451(19) [170 K], 1.32(3) [275 K] 1.471(19) [170 K], 1.35(4) [275 K]	[76]
$K_3[HF_2][Ta(O_2)F_5]\cdot H_2O$	2.011(8) [170 K], 2.007(8) [290 K] 1.873(10) [170 K], 1.886(10) [290 K] 1.955(7) [170 K], 1.957(6) [290 K] 1.948(8) [170 K], 1.943(9) [290 K]	1.936(10) [170 K], 1.925(10) [290 K]	1.443(22) [170 K], 1.389(24) [290 K]	[74]
In $K_6[Ta_3(O_2)_3OF_{13}]\cdot H_2O$				
$[Ta(O_2)F_5]^{2-}$	1.99, 1.89 1.95, 1.95	1.93	1.39	[100]
$[Ta_2O(O_2)_2F_8]^{4-}$	1.98, 1.98 1.96, 2.03 1.96, 1.99	*peroxo*, *μ-oxo* 1.99, 1.86 1.95, 1.93	1.64 1.75	
$(Et_4N)[Ta(O_2)F_4(L)]$ L = 2-methylpyridine *N*-oxide	1.91(3), 1.89(4) 1.96(4), 1.95(4) 1.91(3), 1.89(3) 1.94(2), 2.06(3)	*peroxo*, NO(L) 1.98(3), 2.14(3) 1.84(3), 2.26(4) 1.99(3) 1.85(3)	1.67(5) 1.43(8)	[84]

ments. Moreover, a comparison has been made between the XRD patterns of $Cs_2[Nb(O_2)Cl_5]$ and $Rb_2[Nb(O_2)Cl_5]$ and those obtained for the corresponding oxo-chloroniobates. No distinction can be made between peroxo and oxo species by this technique, the O^{2-} and $O_2{}^{2-}$ ions possessing very close diameters [81,101].

3.2. Halide-free heteroleptic peroxo complexes

3.2.1. General comments

It is possible to substitute, in the tetraperoxometallate species $[M(O_2)_4]^{3-}$, either one peroxo group by one bidentate ligand, or two peroxo groups by (i) two bidentate ligands, (ii) one tridentate ligand and one monodentate ligand or (iii) one tetradentate ligand. In the absence of halides, the substitution of more than two peroxo groups has not been described up to now. Table 3 lists all the halide-free heteroleptic peroxo niobates and -tantalates reported so far in the literature and Fig. 5 displays the metal environment described in the case of such homometallic compounds.

Some homo- and hetero-bimetallic species of Nb and/or Ta have also been obtained with tartaric acid and polyaminocarboxylic acids with high denticity (H_5dtpa, H_6ttha) [25,26,52]. In almost all the halide-free heteroleptic complexes, Nb and Ta display a coordination number of eight. The only exceptions refer to the compounds $[M(O_2)_2(L)]$ [6] and $[Nb(O_2)_2OH(L)]$ [102] with L = hqn, for which a coordination number of six or seven, respectively, has been reported.

These heteroleptic compounds have been prepared in aqueous solution from a precursor of the metal in the presence of H_2O_2 and the ligand L in the appropriate M/L molar ratio. In each case, the niobium and tantalum precursor engaged is the tetraperoxometallate, $[M(O_2)_4]^{3-}$ which is either pre-isolated in the solid state [16,25,26,52,59,103,104] or formed in situ from the dissolution of the alkaline metallate, KMO_3 [102,105,106] or the niobic/tantalic acid in excess H_2O_2 and in the pres-

Table 3
Halide-free heteroleptic peroxo niobate and -tantalate complexes described in the literature with carboxylate, polyaminocarboxylate, *N*-heterocyclic ligands and Schiff bases

Carboxylates	Reference	Polyaminocarboxylates	Reference	*N*-heterocycles	Reference	Schiff bases	Reference
$K_3[M(O_2)_2(ox)_2]\cdot H_2O$	[105]	$K_3[M(O_2)_3(H_2edta)]\cdot nH_2O_2$ ($n \le 1$)	[107]	$K[M(O_2)_3(phen)]$	[105]	$K[Nb(O_2)_2(salen)]\cdot 8H_2O$	[1]
$K_3[Nb(O_2)_2(ox)_2]$	[104]	$(NH_4)_3[M(O_2)_3(H_2edta)]\cdot nH_2O_2$ ($n \le 1$)	[107]	$K[Nb(O_2)_3(phen)]\cdot 3H_2O^*$	[106,111]	$K[Nb(O_2)_2(hnpren)]\cdot 8H_2O$	[1]
$Rb_3[Nb(O_2)_2(ox)_2]$	[104]	$(NH_4)_3[Nb(O_2)_2(edtaO_2)]\cdot H_2O\cdot H_2O_2$	[59]	$K[Nb(O_2)_3(phen)]\cdot 3H_2O\cdot H_2O_2{}^*$	[106,111]	$K[Nb(O_2)_2(haed)]\cdot 8H_2O$	[1]
$Cs_3[Nb(O_2)_2(ox)_2]$	[104]	$(gu)_3[Nb(O_2)_2(edtaO_2)]\cdot 2H_2O$	[59]	$K[M(O_2)_3(bpy)]$	[105]	$K[Nb(O_2)_2(hned)]\cdot 8H_2O$	[1]
$(NH_4)_3[Nb(O_2)_2(ox)_2]$	[16,104]	$(gu)_3[Nb(O_2)_2(edtaO_2)]\cdot 3H_2O\cdot H_2O_2{}^*$	[59]	$K[M(O_2)_2(hq)_2]\cdot 2H_2O_2$	[110]	$K[Nb(O_2)_2(acen)]\cdot 8H_2O$	[1]
$(NH_4)_3[Nb(O_2)_2(ox)_2]\cdot H_2O^*$	[108]	$(gu)_3[Ta(O_2)_2(edtaO_2)]\cdot 2H_2O^*$	[48]	$K[Nb(O_2)_2(hq)_2]\cdot 2H_2O$	[102]	$K[Nb(O_2)_2(salphen)]\cdot 8H_2O$	[1]
$(gu)_3[Nb(O_2)_2(ox)_2]\cdot 2H_2O^*$	[16]	$(gu)_3[Ta(O_2)_2(edtaO_2)]\cdot 2.32\ H_2O\cdot 0.68H_2O_2{}^*$	[48]	$K[Nb(O_2)_2(OH)(hq)]\cdot 2H_2O$	[102]	$K[Nb(O_2)_2(anac)]\cdot 8H_2O$	[1]
$K_3[Nb(O_2)_3(ox)]$	[104]	$(gu)_3[Nb(O_2)_2(pdtaO_2)]^*$	[59]	$[Nb(O_2)_2(hq)]$	[5]	$K[Nb(O_2)_2(salpren)]\cdot 8H_2O$	[1]
$Rb_3[Nb(O_2)_3(ox)]$	[104]	$(gu)_3[Ta(O_2)_2(pdtaO_2)]\cdot H_2O$	[48]	$(gu)_2[Nb(O_2)_3(pic)]$	[103]	$K[Nb(O_2)_2(sac)]\cdot 8H_2O$	[1]
$Cs_3[Nb(O_2)_3(ox)]$	[104]	$(gu)_3[Nb_2(O_2)_4(dtpaO_3)]\cdot 3H_2O$	[26]	$(gu)_2[Nb(O_2)_3(picO)]^*$	[103]	$K[Nb(O_2)_2(sap)]\cdot 8H_2O$	[1]
$(NH_4)_3[Nb(O_2)_3(ox)]$	[104]	$(gu)_3[Ta_2(O_2)_4(dtpaO_3)]\cdot 5H_2O$	[26]	$(gu)_3[Nb(O_2)_3(pzdc)]\cdot H_2O$	[103]	$K[Nb(O_2)_2(hntrien)]\cdot 8H_2O$	[1]
$K_3[M(O_2)_3(H_2cit)]\cdot 2H_2O$	[52]	$(gu)_3[Nb_2(O_2)_4(HtthaO_4)]\cdot 2H_2O$	[26]	$K[M(O_2)_2(H_2O)(dipic)]\cdot 2H_2O$	[52]	$K[Nb(O_2)_2(H_2O)(hphpd)]\cdot 8H_2O$	[1]
$(NH_4)_3[Nb(O_2)_3(H_2cit)]$	[16]	$(gu)_3[Ta_2(O_2)_4(HtthaO_4)]\cdot 3H_2O$	[26]	$[Nb(O_2)_2(OH)(H_2O)(bpy)]$	[105]		
$K_3[M(O_2)_3(H_2tart)]\cdot H_2O$	[52]	$(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot 2.5H_2O$	[26]				
$(NH_4)_3[Nb(O_2)_3(H_2tart)]\cdot 1.5H_2O$	[16]	$(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot 2H_2O$	[26]				
$K_6[M_2(O_2)_6(tart)]\cdot 2H_2O$	[52]						
$(gu)_5[Nb_2(O_2)_4(tart)(Htart)]\cdot 4H_2O^*$	[25]						
$(gu)_6[Ta_2(O_2)_4(tart)_2]\cdot 4H_2O^*$	[25]						
$(gu)_5[NbTa(O_2)_4(tart)(Htart)]\cdot 4H_2O$	[25]						
$K_3[M(O_2)_3(glyc)]\cdot 2H_2O$	[52]						
$K_3[Nb(O_2)_3(Hmal)]\cdot H_2O$	[52]						

* Crystal structures have been solved.

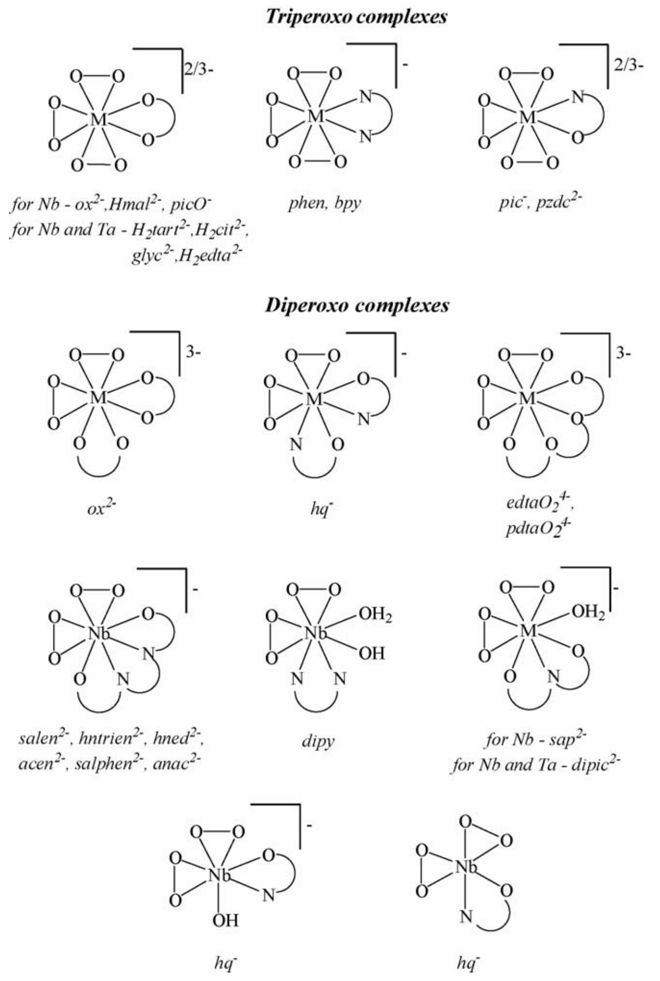


Fig. 5. Environment of the metal atom reported for halide-free homometallic heteroleptic peroxo complexes of niobium and tantalum derived from the corresponding tetraperoxometallate.

ence of a source of the counter-ions [1,59,107]. As far as heterometallic Nb/Ta complexes with H_4tart, H_5dtpa and H_6ttha are concerned, they have been obtained from an equimolar mixture of both tetraperoxometallate and the ligand in the M/L molar ratio equal to 1. Some complexes of formula $[M(O_2)_2(L)]$ have been obtained from Nb or Ta pentachloride and 8-hydroxyquinoline in methanol. Hydrolysis of $K_3[Nb(O_2)_4]$ in acidic medium (H_2SO_4) and in the presence of 2,2′-bipyridine has led to the formation of a diperoxohydroxoaquabipyridine niobium species, $[Nb(O_2)_2(OH)(H_2O)(bpy)]$ [105]. And finally, the oxotrioxalato complex, $(NH_4)_3[NbO(ox)_3]\cdot H_2O$ reacts with hydrogen peroxide to form the corresponding peroxo compound, $(NH_4)_3[Nb(O_2)_2(ox)_2]\cdot H_2O$, by replacing one oxalate ligand by one peroxo group [108].

All these halide-free heteroleptic compounds are soluble in water and insoluble in organic solvents. Their solubility in water can be enhanced by the presence of hydrogen peroxide.

3.2.2. Mononuclear carboxylate complexes

Several anionic peroxo complexes of niobium have been described with the oxalic acid. These compounds contain either two oxalato ligands (ox^{2-}) and two peroxo groups like in the compounds of general formula $(C^I)_3[Nb(O_2)_2(ox)_2]\cdot xH_2O$ ($C^I = K^+$, Rb^+, Cs^+, NH_4^+, gu^+) [16,104,105,108], or one oxalato ligand and three peroxo groups like in the salts $(C^I)_3[Nb(O_2)_3(ox)]\cdot xH_2O$ ($C^I = K^+, Rb^+, Cs^+, NH_4^+$) [104].The tantalum diperoxo complex $K_3[Ta(O_2)_2(ox)_2]\cdot H_2O$ has also been reported [105]. Homonuclear complexes with α-hydroxycarboxylic acids of general formula $(C^I)_3[M(O_2)_3(L)]\cdot xH_2O$ ($C^I = K^+$ or NH_4^+, $L = H_2cit^{2-}$, H_2tart^{2-}, $glyc^{2-}$ and $Hmal^{2-}$) have been described for both metals [16,52].

The thermal stability of the tetraperoxometallate compounds can be enhanced upon substitution of several peroxo groups by carboxylato ligands. For example, the thermal behaviour of the oxalate, citrate and tartrate complexes of niobium has been investigated [16,104]. These compounds decompose slowly to provide, near 600 °C, Nb_2O_5. The oxalate species however gives sometimes rise to an explosion upon rapid heating [104].

The IR and Raman spectra of the peroxo–carboxylato complexes display, in addition to characteristic frequencies of the carboxylato group(s) in the range 1620–1730 and 1350–1450 cm^{-1}, vibrations of the peroxo ligands in the region 820–870 cm^{-1} [16,25,52,104,105]. Two and three ν(O–O) bands are observed in the case of diperoxo and triperoxo species, respectively, and the number of such stretching bands is thus related to the number of peroxo ligands present in the coordination sphere. Moreover, as first mentioned in the case of the tetraperoxometallate, a theoretical interpretation of the experimental observations made by vibrational IR (and also Raman) spectroscopies has been carried out recently on stoichiometric model complexes like the homoleptic $[M(O_2)_4]^{3-}$ but also the heteroleptic $[M(O_2)_3L_2]^{x-}$, *cis* and *trans* $[M(O_2)_2L_4]^{y-}$ and $[M(O_2)L_6]^{z-}$ [60].This study provides the normal modes of vibrations involving peroxo ligands, namely ν(O–O) and $\nu[M(O_2)]$, their corresponding calculated frequency and their activity in IR and/or Raman spectroscopy. The theoretical results from the model complexes are compared with experimental IR and Raman spectroscopic data reported in the literature and the empirical rules stating that the presence of two or three ν(O–O) bands indicates the formation of a diperoxo or triperoxo complex, respectively, have been validated [16,48,59,104]. ^{13}C NMR measurements have been carried out on the peroxo–carboxylato complexes of Nb and Ta. The spectrum of the $[Nb(O_2)_2(ox)_2]^{3-}$ anion displays the presence of two very close peaks suggesting that complexation implies differentiation of the two carbon atoms in both bidentate oxalate ligands [16]. In the case of the $[M(O_2)_3(H_2cit)]^{3-}$, $[Ta(O_2)_3(H_2tart)]^{3-}$ and $[M(O_2)_3(glyc)]^{3-}$ anions, the ^{13}C NMR results suggest that both ligands are bidentate, with binding atoms being oxygen atoms from one carboxylato group and one alkoxo group [52]. Complexation with the metal atom results therefore in a five-membered chelate ring. According to Dengel and Griffith, only carboxylate ligands that allow the formation of this type of chelate ring lead to peroxo–carboxylato complexes of niobium or tantalum. Attempts to synthesize complexes with malonic or succinic acid, which would give six-membered rings, have been unsuccessful [52]. Fig. 6 illustrates the formation of five-membered chelate rings by the bidentate coordination of the oxalato, citrato, tartrato and glycolato ligands to the metal atom.

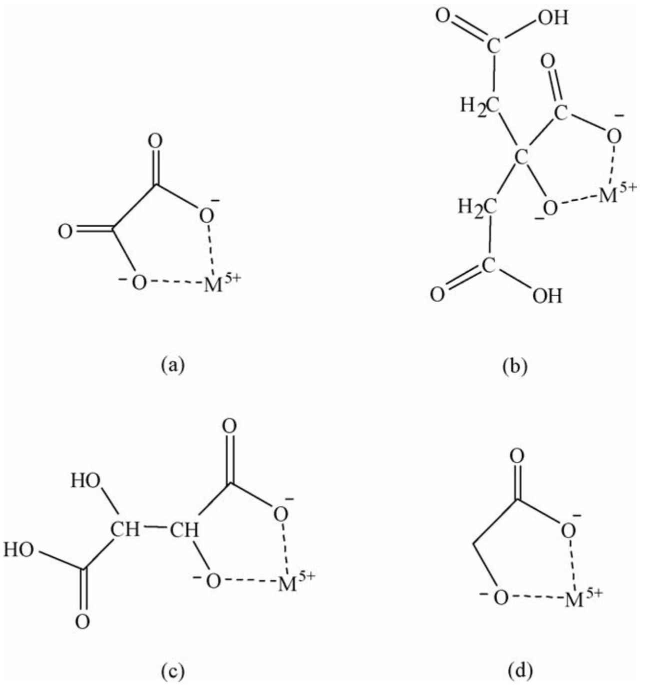


Fig. 6. Bidentate coordination of the (a) oxalato, (b) citrato, (c) tartrato and (d) glycolato ligands in the peroxo–carboxylato Nb and/or Ta compounds, showing the formation of the five-membered chelate rings.

In comparison with their halide-containing analogues, few crystal structures have been resolved for peroxo–carboxylato compounds. XRD measurements have only been carried out on single crystals of the niobium diperoxo-dioxalato derivatives with ammonium and guanidinium cations, of stoichiometry $(NH_4)_3[Nb(O_2)_2(ox)_2]\cdot H_2O$ and $(gu)_3[Nb(O_2)_2(ox)_2]\cdot 2H_2O$, respectively [16,108]. The environment of the metal atom in both compounds is identical. The two bidentate peroxide groups are in *cis* configuration and the coordination polyhedron has been described as a dodecahedron in both cases.

3.2.3. Mononuclear polyaminocarboxylate complexes

Very few papers have reported peroxo complexes of niobium and/or tantalum with polyaminocarboxylate(PAC)-type ligands. Compounds with ethylenediaminetetraacetic acid (H_4edta) have been prepared by Vuletic and Prcic but have been poorly characterized. The stoichiometry $(C^I)_3[M(O_2)_3(H_2edta)]\cdot nH_2O_2$ with $A^I = K^+$ or $NH_4{}^+$ has been proposed only on the basis of chemical analyses and IR spectroscopy data [107]. More recently, similar niobium and tantalum compounds with H_4edta and also with the propylenediaminetetraacetic acid (H_4pdta) have been described [48,59]. The compounds have been obtained by the same method as Vuletic but in that case, the authors have evidenced the in situ oxidation by excess H_2O_2 of the nitrogen atoms of the PAC ligand into bis(*N*-oxide)s. The obtained species correspond to the general formula $(NH_4)_3[Nb(O_2)_2(LO_2)]\cdot xH_2O\cdot yH_2O_2$ and $(CN_3H_6)_3[M(O_2)_2(LO_2)]\cdot xH_2O$ in which H_4LO_2 refers to the bis(*N*-oxide) derivative of the PAC ligand (L = edta, pdta). The same complexes could also been obtained by reacting the tetraperoxometallate with the pre-isolated *N*-oxide derivatives of the starting PAC acids, H_4edtaO_2 and H_4pdtaO_2, which were synthesized independently following a reported procedure [109].

The in situ oxidation of the nitrogen atoms of PAC ligands during the syntheses has been evidenced by the presence, in all IR spectra, of the intense ν(N–O) band at ca. 900 cm^{-1}. Moreover, the IR spectra of theses complexes show systematically two ν(O–O) bands in the range 855–875 cm^{-1}, a spectral shape which evidences the formation of diperoxo species, and bands arising from the PAC ligands like the antisymmetric stretching frequency of the carboxylato groups bound to the metal, ν_{as}(COO), occurring in the range 1610–1650 cm^{-1} [48,59].

Just like the IR spectroscopy, ^{13}C and ^{15}N NMR analyses of these complexes have revealed the oxidation of the *N* atoms in the PAC ligands, from the particularly high chemical shift of both nitrogens and both adjacent carbon atoms. Information on the complexation of the bis(*N*-oxide) ligand has also been provided by ^{13}C NMR. The complete analysis of the ^{13}C spectra has allowed to determine the coordination mode of the ligand to the metal atom: the bis(*N*-oxide)PAC is tetradentate, the four binding atoms being oxygens from two carboxylates (each placed on a different *N* atom) and two *N*-oxide groups [48,59]. These conclusions have been confirmed by X-ray structural analyses of the $(gu)_3[Nb(O_2)_2(edtaO_2)]\cdot 3H_2O\cdot H_2O_2$, $(gu)_3[Nb(O_2)_2(pdtaO_2)]$ [59] and $(gu)_3[Ta(O_2)_2(edtaO_2)]\cdot 2.32\ H_2O\cdot 0.68\ H_2O_2$ [48] compounds. In the molecular anion of each complex, the metal atom is eight-fold-coordinated and is surrounded by a tetradentate $PACO_2$ ligand and two bidentate peroxo groups. The coordination polyhedron has been described as a dodecahedron which is highly distorted on one side. The four oxygen atoms from the peroxo groups are coplanar within experimental errors while, on the opposite side of the polyhedron, the four oxygen atoms from the $PACO_2$ ligand are not coplanar. The structure of the molecular anion $[Nb(O_2)_2(edtaO_2)]^{3-}$ as well as the coordination polyhedron around the niobium atom is drawn in Fig. 7.

3.2.4. Mononuclear complexes with N-containing heterocyclic ligands

Most peroxo complexes described with *N*-containing heterocyclic ligands present a coordination number of eight. Many of them contain in their coordination sphere only peroxo groups and the organic ligand(s). This is the case for the series of compounds of stoichiometry $K[M(O_2)_3(phen)]$ [105], $K[M(O_2)_3(bpy)]$ [105], $K[M(O_2)_2(hq)_2]\cdot 2H_2O_2$ [110], $K[Nb(O_2)_2(hq)_2]\cdot 2H_2O$ [102], $(gu)_2[Nb(O_2)_3(L)]$ (L = pic$^-$ or picO$^-$) [103] and $(gu)_3[Nb(O_2)_3(pzdc)]\cdot H_2O$ [103], in which the heterocyclic ligands are always bidentate via nitrogen and/or oxygen atoms. Some species have been described with a water molecule and/or a hydroxo group bounded to the metal atom, like in $K[M(O_2)_2(H_2O)(dipic)]\cdot 2H_2O$ [52] and $[Nb(O_2)_2(OH)(H_2O)(bpy)]$ [105]. In these cases, the dipicolinato ligand has been described as tridentate and bipyridine as bidentate, so that the eight-fold-coordination is reached for both species. Other peroxo complexes of niobium with the hydroxyquinolinate ligand have been described, $K[Nb(O_2)_2(OH)(hq)]\cdot 2H_2O$ [102] and $[Nb(O_2)_2(hq)]$ [5], and they display coordination numbers of seven and six, respectively. The six-fold coordination is abnormally low for that kind

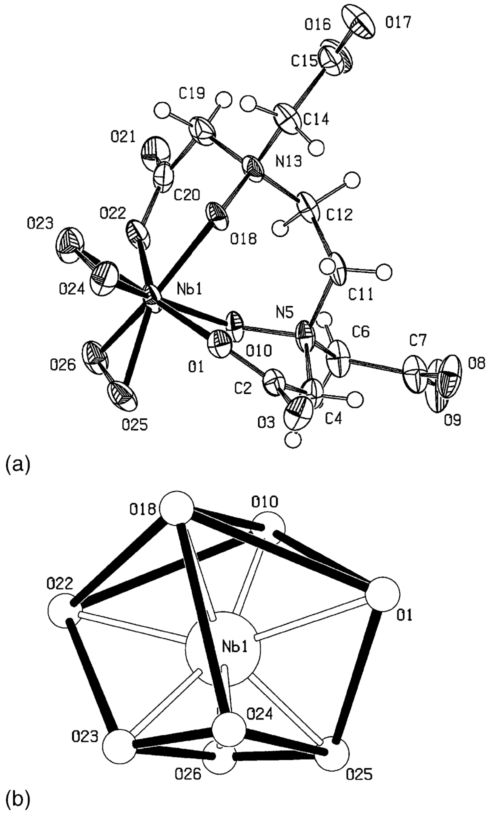


Fig. 7. (a) Molecular structure of $[Nb(O_2)_2(edtaO_2)]^{3-}$ and (b) the coordination polyhedron around the niobium atom. Reproduced from Ref. [48], with permission from copyright owners.

of compounds but this complex has been poorly characterized. Moreover, it has been prepared from $NbCl_5$ and the authors did not check the incorporation of chloride in the coordination sphere, which would be a potential solution for this apparently abnormal coordination number.

Thermal analyses have been performed on the triperoxo compounds $(gu)_2[Nb(O_2)_3(L)]$ (L = pic$^-$ or picO$^-$) and $(gu)_3[Nb(O_2)_3(pzdc)]\cdot H_2O$ [103], which display a degradation in several steps into Nb_2O_5, at a final decomposition temperature of 600–620 °C.

IR spectra of the complexes with *N*-containing heterocyclic ligands have been recorded. Classically, in addition to the vibrations due to the organic ligands, water molecules or hydroxo groups, ν(O–O) bands in the region 820–870 cm^{-1} have been observed. For example, in the case of the diperoxo species $K[NbO_2)_2(H_2O)(dipic)]\cdot 2H_2O$, two such bands occur at 851 and 845 cm^{-1} [52] and in the case of a triperoxo species like $(gu)_2[Nb(O_2)_3(pic)]$, three ν(O–O) vibrations are present at 864, 833 and 819 cm^{-1} [103]. Raman analyses of several compounds have also been carried out, but have led to similar results as IR as far as the peroxo groups are concerned [52].

Mass spectrometry of the $(gu)_2[Nb(O_2)_3(L)]$ (L = pic$^-$ or picO$^-$) and $(gu)_3[Nb(O_2)_3(pzdc)]\cdot H_2O$ complexes displays, in each case, fragments corresponding to the parent ion associated with proton(s) or counter-ion(s), confirming the stoichiometry proposed by the authors [103].

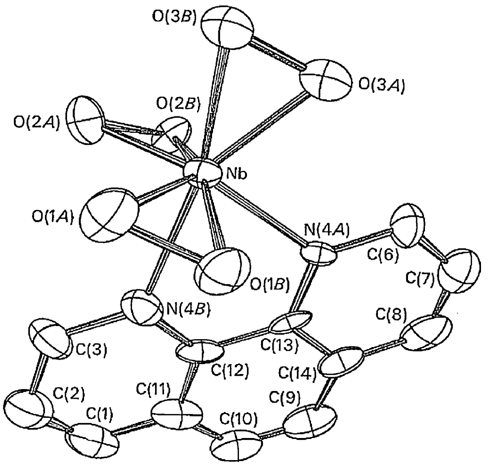


Fig. 8. Molecular structure of $[Nb(O_2)_3(phen)]^-$. Reproduced from Ref. [106], with permission from copyright owners.

The crystal structure of the $K[Nb(O_2)_3(phen)]\cdot 3H_2O$, $K[Nb(O_2)_3(phen)]\cdot 3H_2O\cdot H_2O_2$ and $(gu)_2[Nb(O_2)_3(picO)]$ complexes with the 1,10-phenantroline and picolinate *N*-oxide ligands have been solved [103,106,111]. In each complex, the niobium atom is once more eight-fold-coordinated and surrounded by three peroxo groups and one bidentate heterocyclic ligand. Figs. 8 and 9 display the structures of the molecular anions $[Nb(O_2)_3(phen)]^{3-}$ and $[Nb(O_2)_3(picO)]^{2-}$, respectively. The coordination polyhedron has been reported in the three species as a dodecahedron and the Nb–O(peroxo) mean distances are of 1.987(7), 1.985(6) and 2.002(5) Å for $K[Nb(O_2)_3(phen)]\cdot 3H_2O$, $K[Nb(O_2)_3(phen)]\cdot 3H_2O\cdot H_2O_2$ and $(gu)_2[Nb(O_2)_3(picO)]$, respectively. The O–O mean bond lengths reach, in the same order, 1.489(10), 1.509(6) and 1.502(6) Å.

3.2.5. Mononuclear complexes with Schiff bases

Agarwal et al. have reported the preparation of niobium peroxo complexes with Schiff base ligands [1]. These compounds have been described as potassium salts of diperoxo species with a tri- or tetradentate ligand, $K[Nb(O_2)_2(L)]\cdot 8H_2O$ (L = salen, hnpren, haed, hned, acen, salphen, anac, salpren, sac,

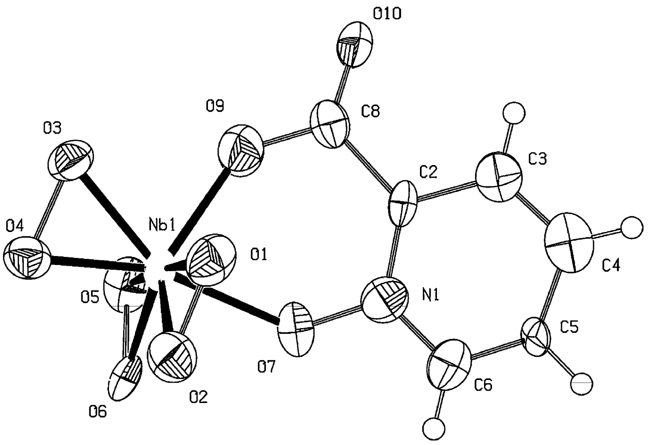


Fig. 9. Molecular structure of $[Nb(O_2)_3(picO)]^{2-}$. Reproduced from Ref. [103], with permission from copyright owners.

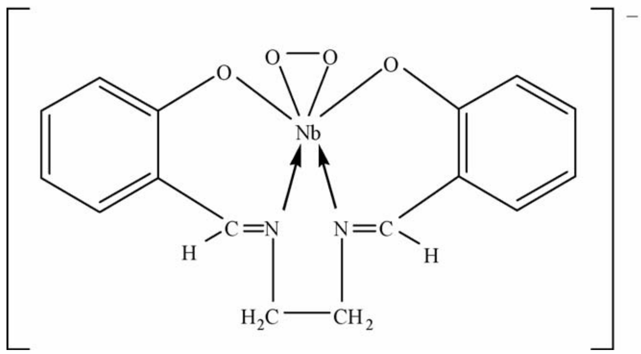


Fig. 10. Proposed structure for the $K[Nb(O_2)_2(salen)]\cdot 8H_2O$ complex [1].

sap and hntrien) and $K[Nb(O_2)_2(H_2O)(hphpd)]\cdot 8H_2O$. The isolated complexes have been poorly characterized and a structure of the salen compound, illustrated in Fig. 10, has been proposed by the authors, assuming the ligand to be tetradentate via its two *N* atoms and its two oxygen atoms from the deprotonated phenol functions.

3.2.6. Dinuclear homo- and heterometallic complexes

Potassium salts of the bimetallic species with tartaric acid, $K_6[M_2(O_2)_6(tart)]\cdot 2H_2O$ have been studied by Dengel and Griffith [52]. In the particular case of these dinuclear complexes, IR and Raman data display bands assignable to peroxo ligands but also vibrations of the tartrate which are similar to those observed for the corresponding Mo(VI) compound, $K_4[MoO_2(O_2)_4(tart)]$ in which the resolved crystal structure revealed the ligand to be bridging and tetradentate [112]. From this comparison, the authors have suggested that, in the $[M_2(O_2)_6(tart)]^{6-}$ anion, each eight-coordinated metal atom carries three peroxo groups and a bridging tartrato ligand. No direct evidence of the heteronuclearity has however been provided.

Dinuclear homobimetallic species with tartaric acid, $(gu)_5[Nb_2(O_2)_4(tart)(Htart)]\cdot 4H_2O$ and $(gu)_6[Ta_2(O_2)_4(tart)_2]\cdot 4H_2O$ [25], and with *N*-oxidized polyaminocarboxylic acids, $(gu)_3[M_2(O_2)_4(dtpaO_3)]\cdot xH_2O$ and $(gu)_3[M_2(O_2)_4(HtthaO_4)]\cdot xH_2O$ [26], as well as their corresponding heterobimetallic complexes, $(gu)_5[NbTa(O_2)_4(tart)(Htart)]\cdot 4H_2O$ [25], $(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot 5/2H_2O$ and $(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot 2H_2O$ [26] have been investigated from a spectroscopic point of view. Their thermal behaviour has also been studied and does not differ significantly from similar mononuclear compounds. TG analyses however have provided valuable information about the heteronuclearity: each analysis displays a slight weight loss corresponding to the last decomposition step, which is characteristic of Nb and Ta compounds. In the case of the homometallic derivatives, this final step appears at 600–610 °C for the niobium derivatives and at 730–750 °C for those of tantalum. In the thermogram of a 1:1 molar ratio mixture of both homometallic compounds, two distinct steps appear at 600–610 and 730–750 °C, in line with the presence of the Nb and Ta homonuclear derivatives, respectively. In the thermograms of the presumed mixed Nb–Ta species, one single step occurs at the intermediate temperature of 680–690 °C, evidencing the heterometallic nature of these compounds [25,26]. Mass spectrometry has also constituted a useful tool for the determination of heteronuclearity. The mass spectra of the heterometallic compounds indeed show fragments containing both metal atoms [25,26]. Moreover, SEM/EDX analyses, performed on numerous monocrystals of $(gu)_5[NbTa(O_2)_4(tart)(Htart)]\cdot 4H_2O$, have proved the presence of both metals in the equimolar Nb/Ta ratio [25]. XRD measurements have also been carried out on these monocrystals as well as on the monocrystals of the corresponding homonuclear complexes. In the molecular structure of the homonuclear $[Nb_2(O_2)_4(tart)(Htart)]^{5-}$ and $[Ta_2(O_2)_4(tart)_2]^{6-}$ (Fig. 11) anions, both tartrato are tetradentate and act as bridging ligands between the metal atoms which are eight-fold coordinated. In both cases, the coordination is completed by two bidentate peroxo groups per metal atoms. The metal-oxygen bond distances obtained for the Nb derivative are not significantly different from those of the Ta complex. Moreover, preliminary XRD measurements realised on crystals of the heteronuclear tartrato compound have revealed that it is isomorphous to its homometallic analogues and no significant difference has been observed in comparison with the experimental parameters obtained for both homometallic complexes [25].

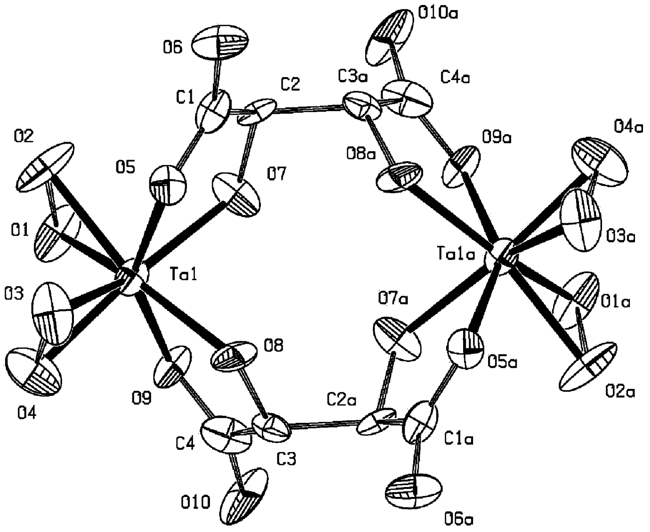
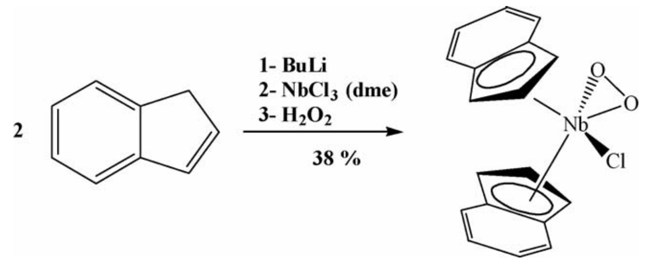


Fig. 11. Molecular structure of $[Ta_2(O_2)_4(tart)_2]^{6-}$. Reproduced from Ref. [25], with permission from copyright owners.

3.3. Organometallic peroxo complexes

Two organometallic peroxo-chloro complexes of niobium have been reported with substituted cyclopentadienyl ligands. Their reported stoichiometry is $(R\text{-}Cp)_2Nb(O_2)Cl$ with R = H or CH_3 [4,113]. These compounds have been prepared from the corresponding dichloro compounds, $(R\text{-}Cp)_2Nb^{I}(V)Cl_2$, which react in CH_2Cl_2 medium with hydrogen peroxide affording the peroxo species. The $(R\text{-}Cp)_2Nb(O_2)Cl$ complexes display two η^5-bounded cyclopentadienyl rings and a η^2-peroxo group, and possess an electronic configuration with 18 electrons and a coordination number equal to 9. The insertion of the peroxo group in the coordination sphere has been evidenced by IR spectroscopy, via the appareance



Scheme 2. Reaction pathway for the bis(η^5-indenyl)chloroniobium(V) peroxide complex [2].

of the ν(O–O) bands near 870 cm^{-1} [4]. Attempts by the authors to synthesize analogous complexes with tantalum, and even vanadium, have been unsuccessful. The crystal structure of the bis(cyclopentadienyl)peroxochloroniobium(V) complex, $(Cp)_2Nb(O_2)Cl$, has been solved [113]. In that organometallic compound, the niobium atom is η^5-bonded to two Cp rings. The two oxygen atoms from the η^2-peroxo group (O–O = 1.47(1) and Nb–O = 1.97(1), 2.00(1) Å) and the chlorine atom (Nb–Cl = 2.483(3) Å) are located in the plane which bisects the $(Cp)_2Nb$ bent sandwich system. The niobium coordination has been described as a pseudotetrahedron consisting of the two centroids of the Cp groups, the peroxo midpoint and the chlorine atom.

Bis(naphtylcyclopentadienyl)-derived niobocene peroxo complexes have also been described by Colletti and Halterman [2]. They obtained the (*R*,*R*)-(+)-bis[2,3-(1,1′-binaphtyl-2,2′-dimethyl)cyclopenta-2,4-dienyl]chloroniobium(V) peroxide (**I**) and bis(η^5-indenyl)chloroniobium(V) peroxide (**II**), from the corresponding niobocene(IV) dichloride and H_2O_2 in inert atmosphere, and from the Nb(III)Cl_3(dme) in the presence of a solution of the indenyl anion at −78 °C, following by addition of H_2O_2 at room temperature, respectively [2]. The one-pot synthesis of the indenyl peroxide species is illustrated in Scheme 2. The first synthesis has provided a final product which shown by ^{1}H NMR analysis to be 90% of peroxide **I** and 10% of niobocene chloro oxide. The proposed structure of compound **I** is drawn in Fig. 12. The IR spectrum of **II** displays a characteristic sharp ν(O–O) band at 860 cm^{-1}, evidencing the η^2 coordination mode for the peroxide group. Due to the presence of a mirror plane which includes both O atoms, the Cl atom and the metal in the node of the plane, both indenyl ligands are equivalent because of C_s-symmetry. The ^{1}H NMR spectrum has thus revealed three different coupled cyclopentadienyl resonances for that complex.

Peroxo-alkyl complexes of permethyltantalocene of general formula $(Cp)_2Ta(O_2)R$ (R = CH_3, C_2H_5, C_3H_7, C_6H_5 and $CH_2C_6H_5$) have been reported and the crystal structure of the compound with R = $CH_2C_6H_5$ has been solved [114]. Exposure of pentane solutions of $(Cp)_2Ta(=X)H$ (X = CH_2, CHC_6H_5, C_6H_5, $CH_2{=}CH_2$, $CH_2{=}CHCH_3$) to 1 atm of dry O_2 leads to precipitation of $(Cp)_2Ta(O_2)R$ upon warming from −80 °C to room temperature. In the structure of the benzyl derivative illustrated in Fig. 13, the arrangement of the peroxo and benzyl ligands in the equatorial plane of the bent sandwich structure is analogous to that reported for the $(Cp)_2Nb(O_2)Cl$ [113].

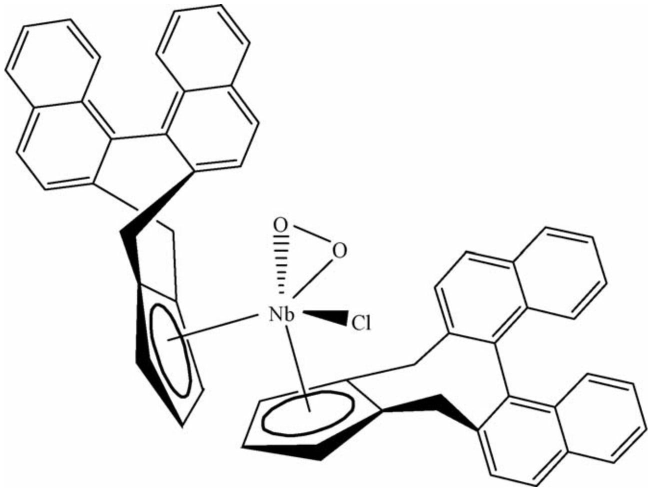


Fig. 12. Proposed structure for the (*R*,*R*)-(+)-bis[2,3-(1,1′-binaphtyl-2,2′-dimethyl)cyclopenta-2,4-dienyl]chloroniobium(V) complex [2].

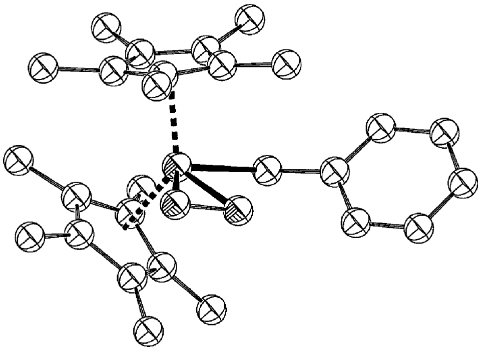


Fig. 13. Structure of $(Cp)_2Ta(O_2)(CH_2C_6H_5)$ (H atoms are omitted) [114].

4. Applications

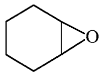
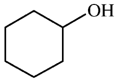
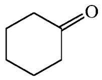
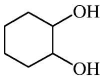
The peroxo complexes of niobium(V) and tantalum(V) are used exclusively in two applications domains: (i) as oxidation catalysts of organic substrates and (ii) as soluble precursors for the preparation of Nb and/or Ta-containing oxides via wet-chemical solution routes.

4.1. Oxidation catalysts

Few papers have reported peroxo compounds of niobium(V) and tantalum(V) as oxidation catalysts of organic and inorganic substrates and they have mostly been published in the last few years [1–6,12].

The tetraperoxoniobate species, as a sodium salt, $Na_3[Nb(O_2)_4]\cdot 13H_2O$ has been used as catalyst in the homogeneous epoxidation of cyclohexene in the presence of hydrogen peroxide as oxidant. As illustrated in Table 4, its catalytic activity in this reaction is quite moderate, while its selectivity in epoxide is particularly good and must be compared with other catalysts giving fair results, as the well-known $Na_2WO_4\cdot 2H_2O$ [3]. While comparing the selectivity of both catalysts in Table 4, we have to keep in mind that the selectivity with respect to epoxidation may be higher for W

Table 4
Comparison of the catalytic performances of the $Na_3[Nb(O_2)_4]\cdot 13H_2O$ complex and the sodium tungstate, $Na_2WO_4\cdot 2H_2O$ in the epoxidation of cyclohexene [3]

Catalyst (%)	Conversion (%)	 (%)	 (%)	 (%)	 (%)
$Na_3[Nb(O_2)_4]\cdot 13H_2O$	7	73	9	16	–
Na_2WO_4	53	42	9	4	42

Reaction conditions: 0.2 mmol catalyst, 10 ml 30 wt.% H_2O_2 (88 mmol), 10 ml *t*-BuOH and 1 ml cyclohexene (9 mmol), 45 °C, 20 h, aging.

peroxo complexes rather than for Nb when the cyclohexene conversion is low, because diol derives from the epoxide ring opening. This compound has also shown some activity for the homogeneous oxidation of alcohols with H_2O_2, and the $[Nb(O_2)_4]^{3-}$ anion, immobilized on a quaternary ammonium polystyrene resin, is much less active in the above two reactions than the homogeneous catalyst [3]. Studies have also been carried out on diperoxo complexes of niobium, of general formula $K[Nb(O_2)_2(L)]\cdot nH_2O$ with Schiff bases ligands (salen, hnpren, haed, hned, acen, salphen, anac, salpren, sac, sap and hntrien) [1]. These species act as active catalysts in oxidation reactions, in the presence of *t*-butyl hydroperoxide, of secondary alcohols and in the epoxidation of cyclohexene, even if in that case, the reaction is not very selective and leads to the formation of cyclohexenol and cyclohexenone. However, they fail to oxidize stoichiometrically the same two substrates. The catalytic performances of these compounds have been compared with that of a oxo porphyrin complex, $[Nb(TPP)]_2O_3$; a competitive oxidation has also been studied between cyclohexene and norbornene, suggesting that the olefins are not coordinated to the metal ion [1].

The organometallic peroxo complexes, $(R\text{-}Cp)_2Nb(O_2)Cl$ with R = H or CH_3 are able to oxidize (i) triphenylphosphine in its corresponding oxide Eq. (3), (ii) sulfur dioxide in sulphate, affording the sulphato complex, $(R\text{-}Cp)_2Nb(SO_4)Cl$ Eq. (4) and (iii) cyclohexene in cyclohexene oxide [4]. In both first cited reactions, oxygen atom(s) from the peroxo group in the complex is (are) transferred to the substrate leading to the corresponding oxo and sulphato complexes, respectively [4]:

$$(R\text{-}Cp)_2Nb(O_2)Cl + PPh_3 \rightarrow (R\text{-}Cp)_2NbOCl + PPh_3O \quad (3)$$

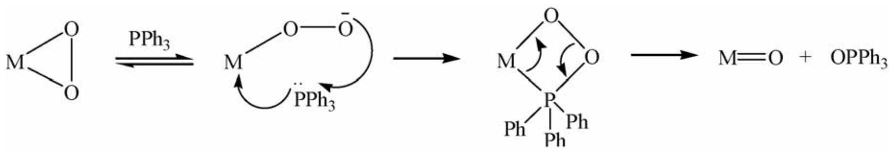
$$(R\text{-}Cp)_2Nb(O_2)Cl + SO_2 \rightarrow (R\text{-}Cp)_2Nb(SO_4)Cl \quad (4)$$

Moreover, these complexes were reported to be inactive towards the oxidation of olefins [4,7,8]. The (*R*,*R*)-(+)-bis[2,3-(1,1′-binaphtyl-2,2′-dimethyl)cyclopenta-2,4-dienyl] chloroniobium(V) peroxide (**I**) and bis(η^5-indenyl)chloroniobium(V) peroxide (**II**) have been tested as catalysts in the enantioselective epoxidation of unfunctionalized alkyl and aryl olefins [2]. For example, the epoxidation of *trans*-3-hexene in acetonitrile in the presence of **I** (0.03%) and H_2O_2 (10%) yields *trans*-3-hexene oxide in 10% enantiomeric excess with 35 turnovers (1.2% yield) [2]. Under identical reaction conditions with cyclohexene, compound **II** produces the epoxidation product only in trace amounts. A comparison is given with the performances of the analogous titanocene compound, (*R*,*R*)-(+)-bis[2,3-(1,1′-binaphtyl-2,2′-dimethyl)cyclopenta-2,4-dienyl] dichlorotitanium [2].

The $[M(O_2)_2L]$ complexes (L = hqn) are very reactive to both organic and inorganic substrates. They oxidize phosphines to their corresponding oxides and olefins to epoxides under stoichiometric conditions while, under catalytic conditions, *trans*-stilbene is converted to α-hydroxyketone [5]. The reaction pathway has been described by the authors in the case of both substrates. Catalytic tests on the oxidation of PPh_3 have also been carried out on $[M(O_2)_2LCl]$ complexes (L = 2-aminopyridine) [6]. The mechanism of oxygen transfer reactions proposed by Tarafder et al. in that reaction is represented in Scheme 3 [5,6].

Peroxo compounds formed in situ have also been reported as catalysts in oxidation reactions but were not isolated in the solid state. For this reason, they have not been included in the previous discussion. Peroxo complexes, formed in solution from $NbCl_5$ in H_2O_2 and in the presence or not of an organic ligand (phosphonic acid or 2,2′-bipyridine), have been tested in the oxidation of benzylic alcohol, in biphasic conditions and in the presence of a phase-transfer catalyst, Bu_4NOH [115]. In most of the experiments in which the H_2O_2 quantity, the ligand nature and the reaction time have been modified, the yield is very good and the major product is benzaldehyde. In some cases, when the oxidant is in excess, small quantities of benzoic acid have been observed.

Finally, some examples of niobium or tantalum complexes, put in the presence of a source of peroxo ligands, have been described as oxidation catalysts but no information about the in situ formation of peroxo species in solution has been given by the authors. Niobium derivatives of $NbCl_3(dme)$ with Schiff bases ligands, chiral or not, have been engaged in the asymmetric oxidation of various sulfides using urea-hydrogen peroxide as



Scheme 3. The mechanism of oxygen transfer reactions in the oxidation of triphenylphosphine by a peroxo species of niobium or tantalum [5,6].

oxidant [116] and the catalytic behaviour of the $[Nb(TPP)]_2O_3$ complex have been evaluated in the oxidation of cyclohexene with hydrogen peroxide and in the presence or not of pyridine, acetic acid or ethanol [117]. Nb-containing mesoporous silicate materials (e.g., MCM-41) or microporous aluminophosphates are also active catalysts in the presence of oxygen donors like H_2O_2 or RO_2H [118–120]. These materials have been tested in the oxidation of thioethers, and the epoxidation of 1-hexene and cyclohexene, but no univocal information about the in situ formation of peroxo Nb species has been reported.

One very interesting application of tantalum peroxo compounds in oxidation catalysis is the asymmetric epoxidation of allylic alcohols [12]. Meunier et al. have tested silica-grafted Sharpless-like tantalum catalysts in the epoxidation of 2-propen-1-ol and *trans*-2-hexen-1-ol, in the presence of *tert*-butanol. These surface tantalum species present good enantioselectivity and activity towards engaged substrates, and display the advantage to be easily separated from the reaction medium by filtration and recycled. The authors have proposed a hypothetical coordination sphere of tantalum for a potential silica-supported active site, in which the metal would bear a η^2-*tert*-butyl peroxo group.

4.2. *Precursors for the preparation of oxides*

Several peroxo complexes of niobium and tantalum have been engaged as precursors in the preparation of oxides. Most of these compounds are indeed water-soluble and air-stable. For this reason, they constitute adequate metal sources for the syntheses of oxide materials in aqueous medium. A particular attention must be paid to their low thermal stability and precautions must often be taken as far as their thermal treatment or calcination is concerned.

4.2.1. *Peroxo precursors formed in situ*

Most of the peroxo species of niobium and tantalum used as precursors of oxides have been obtained in situ, were not isolated at the solid state and often remained poorly characterized. In order to synthesize lead magnesium niobates, some authors have used a solution called "peroxo-niobic", prepared from niobic acid dissolved in excess H_2O_2 medium, without additive [19–21] or in the presence of complexing agents like citric acid [18,23] or H_4edta [22]. An example of preparation of $LiNbO_3$ and $NaNbO_3$ has been recently reported from the peroxo-niobic solution neutralised by LiOH and NaOH, respectively [17]. On the basis of IR and Raman spectroscopies studies in solution, an hypothetical structure of a peroxo-citrato-niobium precursor has been proposed by Narendar and Messing [18]. As drawn in Fig. 14, the complex in aqueous solution would correspond to a dimeric species with each niobium atom bearing an oxo group and a peroxo ligand. Two citrato ligands are also present and both are tetradentate and bridging.

4.2.2. *Molecular peroxo precursors*

Peroxo complexes of niobium, and in a less extended way of tantalum, have been used as molecular precursors of oxides. These compounds, which have been isolated in a solid form and characterized by several techniques, have already been described in Section 3. In order to avoid contamination of the final solid materials by halides or alkali metals, these molecular precursors are halide-free and contain non-metallic counter-ions, that would leave no residue upon thermal degradation.

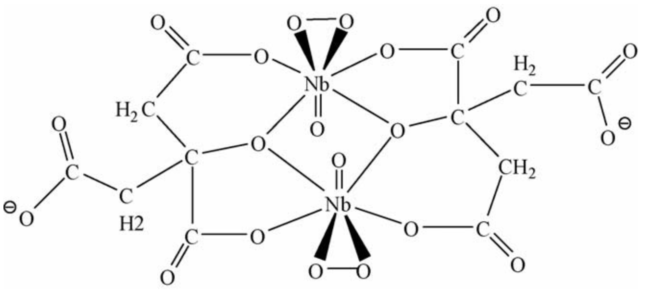


Fig. 14. Proposed molecular structure for the bridged peroxo-citrato niobium complex [18].

High purity and fluorine-free Nb_2O_5 and Ta_2O_5 have been obtained from the hydrolytic decomposition [121] as well as from the thermal treatment [50] of $(NH_4)_3[M(O_2)_4]$. Nb–Mo bulk or silica-supported oxide catalysts have also been prepared from aqueous solutions of peroxo–carboxylato niobium(V) complexes and their analogous compounds of molybdenum(VI). Multimetallic oxides of the three systems Nb–Ta–O, Nb–Ta–V–O and Nb–Ta–Bi–O have been synthesized from pre-isolated water-soluble molecular precursors of the metals involved in the oxide formulation. The complexes which have been considered for niobium and tantalum are the $(gu)_3[Nb(O_2)_2(edtaO_2)]\cdot 2H_2O$ and $(gu)_3[Ta(O_2)_2(edtaO_2)]\cdot 2H_2O$ species [24]. This "molecular precursors method" has allowed to obtained oxides of general formula $(Ta_xNb_{1-x})_2O_5$, $Ta_xNb_{1-x}VO_5$ and $BiTa_xNb_{1-x}O_4$ $(0 < x < 1)$, in quite mild thermal conditions and with particular morphology and textural properties.

When different metals are involved in the oxide formulation, the main advantage of the "molecular precursors method" is the potential use of heterometallic single-source precursors, when available, because they are expected to provide a much greater control of the metal stoichiometry in the final oxide. Recently, the use of binuclear peroxo complexes containing niobium and tantalum has been reported in the context of preparation of Nb–Ta mixed oxides [25,26]. Heterobimetallic peroxo-tartrato and peroxo-PAC complexes, of stoichiometry $(gu)_5[NbTa(O_2)_4(tart)(Htart)]\cdot 4H_2O$ [25], $(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot 5/2H_2O$ and $(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot 2H_2O$ [26] have been used as single-source molecular precursors for the solid solution $NbTaO_5$. An equimolar mixture of the corresponding homometallic precursors has also been engaged in the same method, and the results have been compared.

5. Concluding remarks

Niobium and tantalum belong, with vanadium, to the group 5 of the Periodic Table. As far as vanadium is concerned, its "peroxo chemistry" is very different from that of niobium and tantalum. Unlike these last two elements, vanadium has a strong tendency to form oxo-peroxo species. The great majority of peroxo-type complexes of V(V) described in the literature displays one or more vanadyl bonds [14,15]. In addition, bridging vanadium peroxo derivatives form very easily. In this aspect, vanadium more resembles group 6 elements like molybdenum and tungsten. The peroxide complexes of niobium(V) and tantalum(V) display a quasi identical chemical behaviour. They exclusively contain the O_2^{2-} ligand in the η^2 coordination mode and sometimes co-ligands such as halides, carboxylates, polyaminocarboxylates, *N*-containing heterocycles and Schiff bases. The variety of peroxo compounds of Nb and Ta is broad and many of them have been thoroughly characterized. The crystal structures which have been solved reveal the metal atom to display a seven- or eight-fold coordination and the coordination geometry is described as a pentagonal bipyramid (or more merely as a monocapped octahedron) and as a dodecahedron, respectively.

The applications of such peroxo-type species of niobium(V) and tantalum(V) lie in two main domains: the oxidation catalysis of inorganic and organic substrates and the preparation of oxide materials. In view of the vast range of peroxo compounds described in the literature, their further exploration is likely to be productive and is expected to boost new applications or to improve already known uses.

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References

[1] D.D. Agarwal, A. Kaul, A. Chaturvedi, Indian J. Chem. 34 (1995) 743.
[2] S.L. Colletti, R.L. Halterman, J. Organomet. Chem. 455 (1993) 99.
[3] L.C. Passoni, M.R.H. Siddiqui, A. Steiner, I.V. Kozhevnikov, J. Mol. Catal. A-Chem. 153 (2000) 103.
[4] J. Sala-Pala, J. Roue, J.-E. Guerchais, J. Mol. Catal. A-Chem. 7 (1980) 141.
[5] M.T.H. Tarafder, Orient. J. Chem. 15 (1999) 207.
[6] M.T.H. Tarafder, S.K. Tan, N. Saravanan, G. Mariotto, Orient. J. Chem. 17 (2001) 83.
[7] H. Mimoun, Transition-metal peroxides-synthesis and use as oxidizing agents, in: S. Patai (Ed.), The Chemistry of Functional Groups, The Peroxides, John Wiley and Sons, Chichester, 1983.
[8] H. Mimoun, Israel J. Chem. 23 (1983) 451.
[9] V. Conte, F. DiFuria, G. Modena, J. Org. Chem. 53 (1988) 1665.
[10] V. Conte, F. DiFuria, S. Moro, J. Phys. Org. Chem. 9 (1996) 329.
[11] V. Conte, F. DiFuria, C. Licini, Appl. Catal. A 157 (1997) 335.
[12] D. Meunier, A. Piechaczyk, A. de Mallmann, J.M. Basset, Angew. Chem. Int. Ed. 38 (1999) 3540.
[13] D.C. Crans, L.Q. Yang, T. Jakusch, T. Kiss, Inorg. Chem. 39 (2000) 4409.
[14] D.C. Crans, J.J. Smee, E. Gaidamauskas, L.Q. Yang, Chem. Rev. 104 (2004) 849.
[15] K.H. Thompson, J.H. McNeill, C. Orvig, Chem. Rev. 99 (1999) 2561.
[16] D. Bayot, B. Tinant, M. Devillers, Catal. Today 78 (2003) 439.
[17] V.T. Kalinnikov, O.G. Gromov, G.B. Kunshina, A.P. Kuz'min, E.P. Lokshin, V.I. Ivanenko, Inorg. Mater. 40 (2004) 411.
[18] Y. Narendar, G.L. Messing, Chem. Mater. 9 (1997) 580.
[19] N. Uekawa, T. Kudo, F. Mori, Y.J. Wu, K. Kakegawa, J. Colloid Interf. Sci. 264 (2003) 378.
[20] Y. Yoshikawa, K. Uchino, J. Am. Ceram. Soc. 79 (1996) 2417.
[21] A.L. Costa, C. Galassi, E. Roncari, J. Eur. Ceram. Soc. 22 (2002) 2093.
[22] M.J. Kim, E. Matijevic, J. Am. Ceram. Soc. 77 (1994) 1950.
[23] Y. Narendar, G.L. Messing, J. Am. Ceram. Soc. 80 (1997) 915.
[24] D. Bayot, M. Devillers, Chem. Mater. 16 (2004) 5401.
[25] D. Bayot, B. Tinant, M. Devillers, Inorg. Chem. 44 (2005) 1554.
[26] D. Bayot, M. Degand, M. Devillers, J. Solid State Chem. 178 (2005) 2635.
[27] A. Castro, D. Palem, J. Mater. Chem. 12 (2002) 2774.
[28] T. Okubo, M. Kakihana, J. Alloy. Compd. 256 (1997) 151.
[29] P. Moggi, M. Devillers, P. Ruiz, G. Predieri, D. Cauzzi, S. Morselli, O. Ligabue, Catal. Today 81 (2003) 77.
[30] T. Ushikubo, Catal. Today 57 (2000) 331.
[31] T. Ushikubo, Catal. Today 78 (2003) 79.
[32] P. Viparelli, P. Ciambelli, L. Lisi, G. Ruoppolo, G. Russo, J.C. Volta, Appl. Catal. A 184 (1999) 291.
[33] Y. Mimura, K. Ohyachi, I. Matsuura, Stud. Surf. Sci. Catal. 121 (1999) 69.
[34] H.W. Zanthoff, W. Grunert, S. Buchholz, M. Heber, L. Stievano, F.E. Wagner, G.U. Wolf, J. Mol. Catal. A-Chem. 162 (2000) 435.
[35] T. Katou, B. Lee, D.L. Lu, J.N. Kondo, M. Hara, K. Domen, Angew. Chem. Int. Ed. 42 (2003) 2382.
[36] Z.G. Zou, H. Arakawa, J.H. Ye, J. Mater. Res. 17 (2002) 1446.
[37] A. Butler, M.J. Clague, G.E. Meister, Chem. Rev. 94 (1994) 625.
[38] O. Bortolini, V. Conte, J. Inorg. Biochem. 99 (2005) 1549.
[39] M.K. Harrup, G.S. Kim, H.D. Zeng, R.P. Johnson, D. VanDerveer, C.L. Hill, Inorg. Chem. 37 (1998) 5550.
[40] D.A. Judd, Q. Chen, C.F. Campana, C.L. Hill, J. Am. Chem. Soc. 119 (1997) 5461.
[41] G.S. Kim, D.A. Judd, C.L. Hill, R.F. Schinazi, J. Med. Chem. 37 (1994) 816.
[42] G.S. Kim, H.D. Zeng, D. VanDerveer, C.L. Hill, Angew. Chem. Int. Ed. 38 (1999) 3205.
[43] S.Q. Shi, Y.G. Chen, J. Gong, Z.M. Dai, L.Y. Qu, Trans. Met. Chem. 30 (2005) 136.
[44] C.W. Balke, J. Am. Chem. Soc. 27 (1905) 1140.
[45] C.W. Balke, J. Am. Chem. Soc. 30 (1908) 1637.
[46] A. Sieverts, E.L. Muller, Zeit. anorg. Chem. 173 (1928) 297.
[47] G. Wehrum, R. Hoppe, Z. Anorg. Allg. Chem. 619 (1993) 1315.
[48] D. Bayot, B. Tinant, M. Devillers, Inorg. Chem. 43 (2004) 5999.
[49] G. Haxhillazi, H. Haeuseler, J. Solid State Chem. 177 (2004) 3045.
[50] K.I. Selezneva, L.A. Nisel'son, Russ. J. Inorg. Chem. 13 (1968) 45.
[51] R.N. Shchelokov, E.N. Traggeim, M.A. Michnik, Russ. J. Inorg. Chem. 16 (1971) 211.
[52] A.C. Dengel, W.P. Griffith, Polyhedron 8 (1989) 1371.
[53] H. Haeuseler, M. Wagener, H. Muller, Z. Naturforsch. B 52 (1997) 1082.
[54] J.K. Ghosh, G.V. Jere, Thermochim. Acta 136 (1988) 73.
[55] G. Kozak, V. Raykova, Proceedings of the 26th International Conference of ICT (Pyrotechnics), vol. 47, 1995, p. 1.
[56] V. Belov, L. Avdonina, A. Mikhlin, Ferroelectrics 131 (1992) 63.
[57] G.V. Jere, L. Surendra, M.K. Gupta, Thermochim. Acta 63 (1983) 229.
[58] J.E. Fergusson, C.J. Wilkins, J.F. Young, J. Chem. Soc. (1962) 2136.
[59] D. Bayot, B. Tinant, B. Mathieu, J.P. Declercq, M. Devillers, Eur. J. Inorg. Chem. (2003) 737.
[60] D. Bayot, M. Devillers, D. Peeters, Eur. J. Inorg. Chem. 20 (2005) 4118.
[61] M. Roch, J. Weber, A.F. Williams, Inorg. Chem. 23 (1984) 4571.
[62] J. Weber, M. Roch, A.F. Williams, Chem. Phys. Lett. 123 (1986) 246.
[63] G. Boehm, Z. Krist. 63 (1926) 319.
[64] R.N. Shchelokov, E.N. Traggeim, M.B. Varfolomeev, M.A. Michnik, S.V. Morozova, Russ. J. Inorg. Chem. 17 (1972) 1273.
[65] G. Mathern, R. Weiss, Acta Crystallogr., Sect. B 27 (1971) 1598.
[66] N. Vuletic, C. Djordjevic, J. Less-Common Met. 45 (1976) 85.
[67] A.C. Dengel, W.P. Griffith, Spectrochim. Acta A 43 (1987) 1173.

[68] R. Geetha, P.S. Rao, S. Subramanian, J. Chem. Soc., Dalton Trans. (1991) 3185.
[69] R. Geetha, P.S. Rao, V. Babu, S. Subramanian, Inorg. Chem. 30 (1991) 1630.
[70] G.V. Jere, L. Surendra, S.M. Kaushik, M.K. Gupta, Thermochim. Acta 42 (1980) 115.
[71] G.V. Jere, L. Surendra, S.M. Kaushik, M.K. Gupta, Can. J. Chem. 60 (1982) 1891.
[72] R. Stomberg, Acta Chem. Scand. A 35 (1981) 389.
[73] R. Stomberg, Acta Chem. Scand. A 35 (1981).
[74] R. Stomberg, Acta Chem. Scand. A 36 (1982) 423.
[75] R. Stomberg, Acta Chem. Scand. A 36 (1982).
[76] R. Stomberg, Acta Chem. Scand. A 37 (1983) 523.
[77] W.P. Griffith, J. Chem. Soc. (1964) 5248.
[78] M.C. Chakravorti, S. Ganguly, G.V.B. Subrahmanyam, M. Bhattacharjee, Polyhedron 12 (1993) 683.
[79] J.-Y. Calves, J.-E. Guerchais, J. Less-Common Met. 32 (1973) 155.
[80] J.-Y. Calves, J.-E. Guerchais, J. Fluor. Chem. 4 (1974) 47.
[81] J.E. Guerchais, B. Spinner, R. Rohmer, Bull. Soc. Chim. Fr. (1965) 55.
[82] J. Dehand, J.E. Guerchais, R. Rohmer, Bull. Soc. Chim. Fr. (1966) 346.
[83] J.-Y. Calves, J.-E. Guerchais, R. Kergoat, N. Kheddar, Inorg. Chim. Acta 33 (1979) 95.
[84] J.C. Dewan, A.J. Edwards, J. Chem. Soc., Dalton Trans. (1977) 981.
[85] J.-Y. Calves, J. Sala-Pala, J.-E. Guerchais, Bull. Soc. Chim. Fr. 3/4 (1975) 517.
[86] J.K. Ghosh, G.V. Jere, Thermochim. Acta 114 (1987) 347.
[87] J.K. Ghosh, G.V. Jere, J. Photochem. Photobiol. A-Chem. 40 (1987) 295.
[88] D.F. Evans, W.P. Griffith, L. Pratt, J. Chem. Soc. (1965) 2182.
[89] W.P. Griffith, T.D. Wickins, J. Chem. Soc. A (1968) 397.
[90] E.M. Nour, A.B. El-Sayed, F. Abdel-Rehim, Spectrochim. Acta A 41 (1985) 865.
[91] L. Surendra, D.N. Sathyanarayana, G.V. Jere, Spectrochim. Acta A 38 (1982) 1097.
[92] R. Schmidt, G. Pausewang, Z. Anorg. Allg. Chem. 488 (1982) 108.
[93] J.-Y. Calves, J.-E. Guerchais, Bull. Soc. Chim. Fr. 4 (1973) 1220.
[94] M. Muller, J. Dehand, Bull. Soc. Chim. Fr. 8 (1971) 2843.
[95] E. Wendling, Bull. Soc. Chim. Fr. (1967) 16.
[96] R. Stomberg, Acta Chem. Scand. A 34 (1980) 193.
[97] Z. Ruzic-Toros, B. Kojic-Prodic, Acta Crystallogr., Sect. B 32 (1976) 1096.
[98] Z. Ruzic-Toros, B. Kojic-Prodic, Acta Crystallogr., Sect. B 33 (1977) 692.
[99] Z. Ruzic-Toros, B. Kojic-Prodic, Inorg. Chim. Acta 86 (1984) 205.
[100] W. Massa, G. Pausewang, Z. Anorg. Allg. Chem. 456 (1979) 169.
[101] E. Wendling, Bull. Soc. Chim. Fr. (1967) 5.
[102] V. de Oliveira, R.A.D. San Gil, E.R. Lachter, Polyhedron 20 (2001) 2647.
[103] D. Bayot, M. Degand, B. Tinant, M. Devillers, Inorg. Chim. Acta 359 (2006) 1390.
[104] R.N. Shchelokov, E.N. Traggeim, M.A. Michnik, K.I. Petrov, Russ. J. Inorg. Chem. 17 (1972) 1270.
[105] C. Djordjevic, N. Vuletic, Inorg. Chem. 7 (1968) 1864.
[106] G. Mathern, R. Weiss, R. Rohmer, Chem. Commun. (1970) 153.
[107] N. Vuletic, E. Prcic, Z. Anorg. Allg. Chem. 450 (1979) 67.
[108] G. Mathern, R. Weiss, Acta Crystallogr. Sect. B 27 (1971) 1572.
[109] B. Beltran Porter, M. de Haro Rodriguez, P. Penalver Conesa, Afinidad 33 (1976) 489.
[110] C. Djordjevic, N. Vuletic, Chem. Ind. (1968) 1360.
[111] G. Mathern, R. Weiss, Acta Crystallogr. Sect. B 27 (1971) 1582.
[112] A.C. Dengel, W.P. Griffith, R.D. Powell, A.C. Skapski, J. Chem. Soc. Chem. Commun. (1986) 555.
[113] I. Bkouche-Waksman, C. Bois, J. Sala-Pala, J.-E. Guerchais, J. Organomet. Chem. 195 (1980) 307.
[114] A. van Asselt, M.S. Trimmer, L.M. Henling, J.E. Bercaw, J. Am. Chem. Soc. 110 (1988) 8254.
[115] C.M.D. Batista, S.C.D. Melo, G. Gelbard, E.R. Lachter, J. Chem. Res. 3 (1997) 92.
[116] T. Miyazaki, T. Katsuki, Synlett (2003) 1046.
[117] C.R. Kaiser, M.A. Abdel-Rehim, M.C.S. Machado, E.L.T. Souza, E.R. Lachter, J. Chem. Res. 10 (1998) 708.
[118] M. Hartmann, A.M. Prakash, L. Kevan, Catal. Today 78 (2003) 467.
[119] M. Ziolek, I. Sobczak, A. Lewandowska, I. Nowak, P. Decyk, M. Renn, B. Jankowska, Catal. Today 70 (2001) 169.
[120] M. Ziolek, Catal. Today 78 (2003) 47.
[121] V. Belov, L. Avdonina, A. Mikhlin, Ferroelectrics 131 (1992) 63.