Introduction

The structures of peroxo compounds of Group IV (Ti, Zr, and Hf) and V (V, Nb, and Ta) transition metals in the highest oxidation degree (d^0 electron configuration) have been studied to different extents (Table 1). The best studied are the crystal structures of peroxo complexes of vanadium(V) (about 60 structures) and to a considerably lesser degree, the structures of peroxo complexes of titanium(IV) (13 structures) and niobium(V) complexes. The structural manifestations of the trans effect of multiply bonded peroxo and oxo ligands in monooxomonomoperoxo complexes of vanadium(V) are compared.

© 2004 MAIK “Nauka/Interperiodica”.

9. Mononuclear Hf(IV), Ti(IV), and V(V) Complexes with tert-butylperoxo Ligands

10. Geometrical Parameters of $M(O_2)_n$ Fragments in Peroxo Complexes of Group IV and V Metals

Conclusions

INTRODUCTION

The structures of peroxo compounds of Group IV (Ti, Zr, and Hf) and V (V, Nb, and Ta) transition metals in the highest oxidation degree (d^0 electron configuration) have been studied to different extents (Table 1). The best studied are the crystal structures of peroxo compounds of vanadium(V) (about 60 structures) and to a considerably lesser degree, the structures of peroxo complexes of titanium(IV) (13 structures) and niobium(V) complexes. The structural manifestations of the trans effect of multiply bonded peroxo and oxo ligands in monooxomonomoperoxo complexes of vanadium(V) are compared.

© 2004 MAIK “Nauka/Interperiodica”.

<table>
<thead>
<tr>
<th>$M$</th>
<th>Total</th>
<th>$M:O_2 = 1:1$</th>
<th>$M:O_2 = 1:2$</th>
<th>$M:O_2 = 1:3$</th>
<th>$M:O_2 = 1:4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>13+1*</td>
<td>12+1*</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>0+1*</td>
<td>0+1*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hf</td>
<td>60+1*</td>
<td>34+1*</td>
<td>24</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>13</td>
<td>8</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Nb</td>
<td>5</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Altogether</td>
<td>91+3*</td>
<td>58+3*</td>
<td>28</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

* Number of structurally characterized tert-butylperoxo complexes of Group IV and V metals.
** Of the total number of 60 peroxo complexes of vanadium(V), 58 are related to oxoperoxo compounds containing VO(O_2)_n complexes, n = 1, 2.
The structural characteristics of oxoperoxo complexes of vanadium(V) with the coordination sites VO(\(O_2\))\(_n\)A\(_m\) (where A are the donor atoms of mono and polydentate ligands, \(n = 1, 2, m = 1–4\)) were analyzed in detail for 58 compounds of this class that were structurally characterized before 2002 in [3, 4], the structures of vanadium(V) oxo peroxo complexes are only briefly considered in our article.

In all the peroxo compounds of Group IV and V metals considered in the present review, the dioxygen ligands coordinate \(M\) atoms in the bidentate–chelating mode. In these cases, the peroxo complexes are characterized by eightfold (dodecahedral), sevenfold (pentagonal-bipyrudal or, in some rare cases, one-capped trigonal-prismatic), or sixfold coordination (tetragonal–pyramidal with a split axial vertex). A particular location is occupied by the complexes of the \((\eta^5-Cp)_2M(\(O_2\))\(_n\)A type (\(\eta^5-Cp = \text{C}_5\text{H}_5\) and \(\text{C}_6\text{Me}_5\); where \(A\) is a monodentate ligand) in which the coordination number of a metal atom equals five or nine, depending on the interpretation of the \(Cp\) ligand as either a monor tridentate one.

If one assumes that the \(O_2\) ligand bonded to a metal in the \(\eta^2\)-mode occupies one coordination site, then the \(V(\(O_2\))\(_n\)A\(_m\) complexes may have four variants of the coordination site: pseudooctahedral \((n = 1, m = 5; n = 2, m = 4)\), pseudotetragonal–pyramidal \((n = 1, m = 4)\), pseudotrigonal–pyramidal \((n = 3, m = 2)\), and pseudotetrahedral \((n = 4, m = 0)\) (scheme 1).

1. TITANIUM(IV) PEROXO COMPLEXES WITH Ti : \(O_2 = 1 : 1\)

Table 2 lists the geometrical parameters of twelve structurally studied titanium(IV) peroxo compounds (I–XII) [5–15].

1.1. Pseudooctahedral Mononuclear Peroxo Complexes of Ti(IV)

Mononuclear complexes of titanium(IV) with the pseudooctahedral coordination of the metal atom are represented by seven examples (I–VII) in Table 2.

In three compounds (I–III), the coordination sphere of the Ti atom includes, in addition to the peroxo ligand, four donor atoms (2 N, 2 O, N, and 3 O or 4 N) from two equivalent or different bidentate–chelating ligands in the \(cis\) positions with respect to each other and one donor atom (O or N) of the monodentate ligand.

In the dimer and polymer oxoperoxo complexes of vanadium(V), the \(O_2\) ligand in a number of cases coordinates metal atoms in the bidentate–chelating–bridging mode (\(\eta^2, \mu\)-mode) [4].

The VO(\(O_2\))\(_2\) complexes may also have the sixfold pentagonal–pyramidal coordination.

The complexes of the \((\eta^5-Cp)_2M(\(O_2\))\(_2\) type may also be considered as pseudotetrahedral if one assumes that the \(Cp\) ligand occupies one site in the coordination polyhedron of the metal.

The \((\text{NH}_3)_2[\text{Ti}(\text{O}_2)\text{F}_3]\) structure is considered in Sect. 2.1 together with the structures of pentfluoroperoxoniobates(V) and pentfluorotantalates(V), \([\text{M}(\text{O}_2\text{F})_5]^{12-}\), \(M = \text{Nb, Ta}\).

---

1 The only exception is the structure of one hafnium \(\text{tert-butylperoxide}\) \([\eta^5-\text{C}_5\text{Me}_5\text{H}(\text{tert-BuOO})(\text{Et})]\) (see Sect. 9).