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Synthesis and characterization of homo- and heterobimetallic niobium^V and tantalum^V peroxo-polyaminocarboxylato complexes and their use as single or multiple molecular precursors for Nb–Ta mixed oxides

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Abstract

New water-soluble bimetallic peroxo complexes of niobium^V and/or tantalum^V with high-denticity polyaminocarboxylate ligands have been prepared, characterized from the spectroscopic point of view, and used as molecular precursors for Nb–Ta mixed oxides. Four new homobimetallic complexes, $(gu)_3[Nb_2(O_2)_4(dtpaO_3)]\cdot 3H_2O$ **1**, $(gu)_3[Ta_2(O_2)_4(dtpaO_3)]\cdot 5H_2O$ **2**, $(gu)_3[Nb_2(O_2)_4(HtthaO_4)]\cdot 2H_2O$ **4** and $(gu)_3[Ta_2(O_2)_4(HtthaO_4)]\cdot 3H_2O$ **5** and the corresponding heterometallic complexes, $(gu)_3[NbTa(O_2)_4(dtpaO_3)]\cdot 2.5H_2O$ **3** and $(gu)_3[NbTa(O_2)_4(HtthaO_4)]\cdot 2H_2O$ **6** have been obtained. In these compounds, the in situ oxidation of the nitrogen atoms of the PAC ligands into N-oxide groups has been evidenced by IR spectroscopy and mass spectrometry. The thermal treatment of the homonuclear complexes in air at 700 or 800 °C, depending on the Ta content, provided Nb_2O_5 or Ta_2O_5 while the heteronuclear compounds led to the solid solution $TaNbO_5$. BET and SEM measurements have been carried out and comparison of the morphology of the samples prepared from homo- and heterometallic precursors is discussed.

Keywords: Niobium; Tantalum; Polyaminocarboxylate; Peroxo complexes; Precursors; Mixed oxides

1. Introduction

In recent years, multimetallic Nb-containing oxides have generated considerable interest in many fields, because of their attractive physical properties: for example, such oxides are widely studied as ferroelectric and piezoelectric materials like $BiNbO_4$ [1], as ion conductors like Y_3NbO_7 [2], and also as promising catalysts in several highly challenging processes, like water photodecomposition [3–8], alkane oxidation or ammoxidation [9,10]. Within the same context, analogous Ta-based oxides, like $BiTaO_4$ [6,11] and $TaVO_5$ [12], were also reported but in a very less extended way than for niobium. The literature describes mainly solid solutions between niobium and tantalum pentoxides, of general formula $(Ta_xNb_{1-x})_2O_5$ [13–15]. Such materials are mainly studied as photocatalysts for water decomposition [3–5].

The conventional way to prepare oxide materials is based on solid-state reactions between the binary oxides. This so-called "ceramic method" requires heat treatments at a relatively high temperature, as well as repeated grinding procedures, and generally results in oxides of low purity. Because of these limitations, alternative routes such as sol-gel synthesis, citrate method, metal-organic chemical vapor deposition (MOCVD) or pyrolytic decomposition are often considered. These methods, requiring metal-organic precursors which have specific chemical and physical

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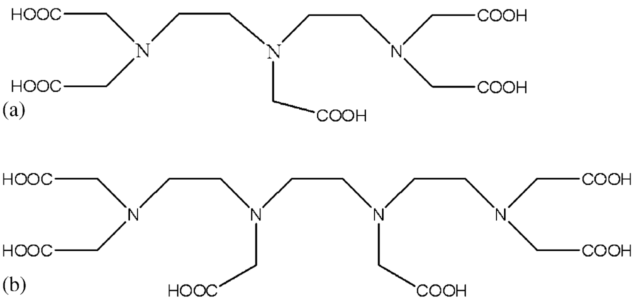
properties, present some obvious advantages: (i) the use of molecular precursors provides homogeneous materials; (ii) these "precursor routes" allow to form crystalline oxides under conditions significantly milder than those employed in conventional solid-state synthesis [16,17] and result in materials with relatively high specific surface areas and (iii) the presence of bridging or chelating organic ligands in the precursors has been shown to avoid unwanted metal segregation during oxide formation [18]. More particularly, when different metals are involved in the final oxide formulation, the main advantage of such routes is the potential use of heterometallic single-source precursors, when available. A single-source precursor provides a direct route to advanced materials and may lead to a higher quality of products because of a much greater control of the metal stoichiometry in the final oxide [19–21]. Ideally, heteronuclear precursor complexes containing the number of metal atoms corresponding to the stoichiometry of the desired oxide phase are required to optimize the approach but this often represents an ambitious challenge.

The Nb- or Ta-based heterometallic compounds described so far are practically exclusively alkoxide-type precursors which, unfortunately, present several disadvantages such as their moisture sensitivity or expensiveness. The described heterometallic complexes of Nb or Ta with oxo and/or alkoxo ligands only are numerous. Compounds such as $Nb_2(OMe)_2(ReO_4)_2$, $M_2O_2(OMe)_{14}(ReO_4)_2$ (M = Nb or Ta) [22], $Mg[Nb(OEt)_6]_2 \cdot 2EtOH$, $Sr[Ta(OiPr)_6]_2 \cdot 2Pr^iOH$ [23], $Mo_4M_2O_8(O^iPr)_{14}$ and $Mo_4M_4O_{16}(O^iPr)_{12}$ (M = Nb or Ta) [24] have been reported recently. Next to that, it has been shown that the association of the metal alkoxides with ligands such as halides, acetate, carboxylates or β-diketonates can be considered as a way to overcome the difficulty of handling them. Several acetato-alkoxo-based heterometallic compounds with Nb such as $MNb_2(OAc)(O^iPr)_{10}$ (M = Mg, Cd or Pb) [18,25] have been studied as precursors for the corresponding MNb_2O_6 phase. Also, some acetylacetonate derivatives such as $M_2^{II}M_2^{V}(acac)_2(OMe)_{12}$ (M^{II} = Co, Ni, Zn or Mg and M^V = Nb or Ta) [26] are known. Moreover, very recently, two heterometallic Nb or Ta and Bi-based compounds with salicylate ligands, $Bi_2M_2(\mu\text{-}O)(sal)_4(Hsal)_4(OEt)_2$ and $BiM_4(\mu\text{-}O)_4(sal)(Hsal)_3(O^iPr)_4$ [20,21], have been reported as single-source precursors for the ferroelectric $BiMO_4$ phase. However, only two mixed niobium and tantalum heterometallic alkoxide-type complexes have been described so far: the homoleptic $NbTa(OMe)_{10}$ compound [27] and the heteroleptic $[Ta(O^iPr)_4]Nb(tea)$ compound (tea = triethanolamine) [28].

We reported very recently the synthesis and characterization of a mixed Nb–Ta peroxo-tartrato complex of stoichiometry $(gu)_5[NbTa(O_2)_4(tart)(Htart)] \cdot 4H_2O$, in which the tartrate is a tetradentate and bridging ligand. This compound displays the advantages to be air-stable and water-soluble and it was engaged as a single-source precursor for the $TaNbO_5$ phase [29].



Scheme 1. Structures of the (a) H_5dtpa and (b) H_6ttha ligands.

In addition, we also studied water-soluble peroxo Nb^V or Ta^V mononuclear complexes with polyaminocarboxylato ligands like ethylenediaminetetraacetic (edta) and propylenediaminetetraacetic (pdta) acids, for which the synthesis in the presence of excess H_2O_2 was shown to lead to an in situ oxidation of both nitrogen atoms of the PAC ligand into N-oxide groups [30,31].

We report here the synthesis and characterization of novel air-stable and water-soluble homo- and heterobimetallic peroxo complexes of Nb^V and Ta^V with polyaminocarboxylato ligands which display a higher denticity than edta and pdta, such as diethylenetriaminepentaacetic (dtpa) and triethylenetetraaminehexaacetic (ttha) acids. The structures of both ligands are illustrated in Scheme 1. They possess a high number of coordination sites, eight and ten, respectively, and therefore could lead to the formation of polynuclear complexes. We expected the in situ N-oxidation of the ligand as previously observed in the case of the edta and pdta species [30,31]. Next to that, the formation of a solid solution between Nb_2O_5 and Ta_2O_5 from the thermal decomposition of the prepared complexes is also investigated.

2. Experimental

2.1. General procedures

The peroxo-polyaminocarboxylato Nb^V and/or Ta^V complexes were prepared by substituting peroxo groups by a polyaminocarboxylate (PAC) ligand in the tetraperoxometallate anion(s), $[M(O_2)_4]^{3-}$. These syntheses were processed in the presence of excess hydrogen peroxide and led, as expected, to the direct formation of the N-oxide derivative of the PAC ligand. This in situ N-oxidation phenomenon was actually previously observed in the case of the edta or pdta peroxo complexes of niobium or tantalum [30,31]. Moreover, the (N-