Alkoxide complexes of Rhenium, Niobium and Tantalum

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Abstract

This thesis describes two major methods for preparation of new mono-, bi- and trimetallic complexes on the basis of Rhenium, Niobium and Tantalum: (1) - the electrochemical method for the synthesis of $Re_4O_4(OEt)_{12}$ and (2) - the interaction of Rhenium heptoxide, Re_2O_7, with alkoxo-derivates of Niobium and/or Tantalum, $M_2(OR)_{10}$ for the synthesis of bi- and trimetallic complexes of common formula $(M_{1-x}M'_x)_4O_2(OR)_{14}(ReO_4)_2$ ($M = Nb; M' = Ta; R = Me, Et$), where x = 0–1. The structures of these complexes were determined by single-crystal X-ray diffraction. The products were also characterized by IR, NMR and X-ray powder diffraction.

The influence of the increasing ligand size on the solubility and stability of the complexes $Re_4O_4(OEt)_{12}$ and $M_4O_2(OR)_{14}(ReO_4)_2$ (M = Nb, Ta; R = Me, Et) has been established. The effect of the ligand and metal ion ratio on the conditions and the chemical composition of the products of thermal treatment have been investigated.

Nanosized Rhenium metal particles (approximately 3 nm in diameter) were obtained from $Re_4O_4(OEt)_{12}$ by thermal decomposition in inert atmosphere at as low temperature as 380 °C.

Semi-ordered macro porous monoliths with the pore size in the range 100 – 250 nm, with the crystal structure related to the block structures of the *L*-modification of Ta_2O_5, were produced from trimetallic complexes of the common formula $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$ (x = 0.3, 0.5, 0.7) via thermal decomposition in air at the temperatures ≤ 1000 °C.

The thermal decomposition in dry nitrogen atmosphere provides formation of solid solutions, which possess the structures related to the block structure of the *H*-modification of Nb_2O_5 for the Niobium-rich precursors and block structure of the *L*-modification of Ta_2O_5 for Ta:Nb $\leq$ 1:1 at the temperatures ≤ 1000 °C.

Keywords: alkoxide, Rhenium, Niobium, Tantalum, nanomaterials, semi-ordered macro porous materials, single-crystal X-ray diffraction, SEM.

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Dedication

To my parents, husband and lovely son.

If person has entered to the bottom level he certainly will step on the top one…

F. Dostoevsky

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Nikonova O.A., Jansson K., Kessler V. G., Sundberg M., Baranov A.I., Shevelkov A.V., Drobot D.V., Seisenbaeva G. A. (2008). Electrochemical Synthesis, Structural Characterization and Decomposition of Rhenium Oxoethoxide, $Re_4O_4(OEt)_{12}$. Ligand Influence on the Structure and Bonding in the High-Valent Tetranuclear Planar Rhenium Alkoxide Clusters. *Inorganic Chemistry* 47, 1295-1300.

II Nikonova O.A., Kessler V.G., Seisenbaeva G.A., Drobot D.V., Shcheglov P.A. (2007). Synthesis and X-ray Single Crystal Study of Niobium and Tantalum Oxo-Ethoxo-Perrhenates $M_4O_2(OEt)_{14}(ReO_4)_2$. *Polyhedron* 26(4), 862-866.

III Nikonova O.A., Seisenbaeva G.A., Kessler V.G., Shcheglov P.A., Drobot D.V. (2007). Comparative Study of Bimetal Alkoxo Complexes of Rhenium, Niobium and Tantalum by Single-Crystal X-ray Diffraction and IR Spectroscopy. *Russian Journal of Inorganic Chemistry* 52(11), 1687-1692.

IV Nikonova O.A., Kessler V.G., Seisenbaeva G.A. (2008). Substitution Features in the Isomorphous Replacement Series for Metal-Organic Compounds $(Nb_xTa_{1-x})_4O_2(OMe)_{14}(ReO_4)_2$, $x = 0.7, 0.5, 0.3$—Single-Source Precursors of Complex Oxides with Organized Porosity. *Journal of Solid State Chemistry* 181(12), 3294-3302.

1 Introduction

The research within this thesis is focused on the synthesis and characterization of a new generation of mono-, bi- and trimetallic complexes on the basis of Rhenium, Niobium and Tantalum, and on production of functional nanostructures and porous materials based on abovementioned metals for potential applications in catalysis.

1.1 Application of Rhenium, Niobium and Tantalum and their compounds

1.1.1 Rhenium

Rhenium and its compounds such as sulphides, oxides, alloys and carbonyl complexes have found application as catalysts in petroleum production, different organic syntheses and radiotherapy.

Rhenium metal is broadly used as a component of catalysts for alkylation in organic synthesis and for industrial processes such as reforming of petroleum feedstock and metathesis of alkenes (Mol J.C. 2004; Xiao J. *et al.,* 1995; Guryev Yu. V. *et al.,* 2007). These catalysts have shown good activity in the hydrocarbon cracking and selective hydrogenation, hydrodesulphurization of heavy crude oil and also selective dehydroaromatization of methane and ethane to benzene (Laurenti D. et al., 2008; Okal J. et al., 1998; Escalona N. et al., 2007; Räty J. et al., 2000; Escalona N. et al., 2002, Escalona N. et al. 2007; Wang L. et al., 2000; Shu Y. et al., 2003; Wang L. et al., 2003). Moreover, Re-containing catalysts show high performance for selective oxidation of methanol and ethanol (Chang Ally S. Y. et al., 2004; Yuan Y. et al., 2000; Tsoncheva T. et al., 2007). Recently, it was discovered that Rhenium/zeolite catalyst is very active in the selective oxidation of benzene to phenol (Kusakari T. et al., 2004).

Rhenium heptoxide, Re_2O_7, has shown high catalytic activity in olefin metathesis and is the only catalyst, which can work efficiently at room temperature (Salameh A. *et al.*, 2008). Moreover, this heterogeneous catalyst can also be used to convert oleate esters when activated by organic derivates of Tin, which use, however, is detrimental to the regeneration process (Mol J. C. *et al.*, 2004). Re_2O_7 dispersed on mesoporous alumina (abbreviated as meso-Al_2O_3) with a narrow pore-size distribution centered at 3 nm has shown higher catalytic activity in the metathesis of internal as well as terminal olefins without functional groups than Re_2O_7 on common γ–Al_2O_3 in liquid phase (Onaka M. *et al.*, 2002; Bakala P.C. *et al.*, 2008). Rhenium oxide supported on ordered mesoporous alumina has even been claimed as more active and selective catalyst than $Re_2O_7/\ \gamma$–Al_2O_3 for alkene metathesis (Oikawa T. *et al.*, 2004).

The most efficient catalyst based on Rhenium is the well-known methyltrioxorhenium (CH_3ReO_3, MTO). This catalyst is particularly useful in oxidation chemistry and shows high activity for epoxidations, C-H and Si-H oxidations but it can also be applied in other types of catalytic reactions such as olefin metathesis and aldehyde olefinations (Jain K.R. *et al.*, 2007; Salameh A. *et al.*, 2007; Mandelli D. *et al.*, 2001; Buffon R. *et al.*, 1992; Buffon R. *et al.*, 1992).

Rhenium complexes, in particular, of the type *fac*-$[Re(L)(CO)_3Cl]$ (where L is a bidentate ligand such as 2,2'-bipyridyl or two monodentate ligands such as 4,4'-bipyridyl), was used as heterogeneous catalyst in the reduction of CO_2 (Scheiring T. *et al.*, 1997; Cecchet F. *et al.*, 2006; Chen Y. *et al.*, 2009). Furthermore, complexes with common core *fac*-$[Re(L)(CO)_3]$ configuration, where L is a ligand, are used in radio pharmacology as analogs to *fac*-$[^{99m}Tc(L)(CO)_3]$-based radiopharmaceuticals (Christoforou A.M. *et al.*, 2007; Anaya S.A.S. *et al.*, 2008).

Rhenium and Molybdenum oxo methoxide complexes $Re_2O_3(OMe)_6$, $ReMoO_2(OMe)_7$ and $MoO_2(OMe)_8$ are used as precursors to prepare highly dispersed mono- and bimetallic oxide species, which were supported on the micro porous NaY zeolite and mesoporous SiO_2 and Al_2O_3. It should be mentioned, that oxomethoxo complexes of Re and Mo loose their ligands when loaded into the micro porous NaY zeolite, so that just metal sub oxide cores, ReO_3 and MoO_3, remain in the intracrystalline voids and reside there as nanosized particles. The obtained clusters reveal both acidic and redox properties (Kustov A.L. *et al.*, 2004; Kustov A.L. *et al.*, 2004).

1.1.2 Niobium and Tantalum

Niobium and Niobium-based compounds find many technological applications, for instance, as oxygen sensors (Rosenfield D. *et al.*, 1996), waveguides (Saito Ya. *et al.*, 1992), or as tunnel barriers in Josephson tunnel junctions (Halbritter J., 1987). Niobium has an excellent corrosion resistance in mineral acids at ambient conditions, except in hydrofluoric acid, but in extremely corrosive media, like concentrated acids and/or at high temperature, Niobium is appreciably attacked. On the contrary, Tantalum is practically unaffected in all acidic solutions, even concentrated and hot (Robin A. *et al.*, 2000). Alloys of these two metals with such metals as Ni and Re, provide most corrosion resistive materials (Vinet B. *et al.*, 2003; Mugishima T. *et al.*, 2006; Cui Y. *et al.*, 1999; Liu Z.-K. *et al.*, 2000). There are a significant number of Niobium-based materials, for example, $NbCl_5$, NbF_5, NbH_x, NbS_2, NbN, NbC, NbO_x and Nb organ metallic compounds which are effective catalysts for many reactions (Tanabe K., 2003). Recently, it was found out that $TaCl_5$ and $Ta(OEt)_5$ are good catalysts for selective synthesis of sulfoxides and sulfones (Kirihara M. *et al.*, 2009). The Niobium oxide coated mesoporous materials as well as Tantalum oxide supported on different mesoporous molecular sieves have found broad application as catalysts for oxidation of methanol (Sobczac I. *et al.*, 2008; Feliczak A. *et al.*, 2009), for the synthesis of vegetable oil-based products (Jehng J.-M. *et al.*, 2007), for propene epoxidation (Held A. *et al.*, 2009) and showed very high selectivity in formaldehyde production from methanol (Trejda M. *et al.*, 2008).

The pentoxides of Niobium and Tantalum, Nb_2O_5 and Ta_2O_5, are used in optical applications as high index and low loss materials for optical waveguides, interference filters, anti-reflective coating (for example in solar cells) (Masse J.-P. *et al.*, 2006).

Niobium and Tantalum oxides have been reported to remarkably enhance catalytic activity and selectivity and to prolong catalytic life when a small amount of the oxides was added to known catalysts (Ushikubo T., 2000). Application of Niobium and Tantalum oxides as matrices in the *in situ* synthesis of Rhenium oxide-based nanocomposites can offer a cost-efficient approach to materials with enhanced stability to reduction. In the literature, there are recent works on Rhenium-based catalysts for the metathesis of olefins CH3ReO3/Nb2O5 (Buffon R. *et al.*, 1992; Buffon R. *et al.*, 1992; Buffon R. *et al.*, 1997), which showed high catalytic activity for metathesis of 1-pentene (Buffon R. *et al.*, 1992). Tantalum pentoxide has also found broad application as oxide support. The redox activity and selectivity of various surface metal oxides such as Re_2O_7, Nb_2O_5, WO_3,

MoO_3 on Ta_2O_5 reflect the natural redox properties of these pure metal oxides and the more active surface redox sites minimized the contribution from the surface acidic sites of the Ta_2O_5 support (Chen Y. *et al.*, 2003). Tantalum composite catalyst has also been used for esterification reaction of lauric acid with ethanol, an important pre-treatment step in the production of bio diesel from renewable feed stocks (Xu L. *et al.*, 2008).

Tantalum and Niobium pentoxides are also used themselves as photocatalysts for different processes such as: cleavage and purification of water (Stodolny M. *et al.*, 2008; Prado A. G.S. *et al.*, 2008; Nakajima K. *et al.*, 2005) and oxidation of organic contaminants (Esteves A. *et al.*, 2008), oxidation of alkanes (Ushikubo T., 2003), partial oxidation of thiols to produce valuable synthons in pharmaceutical and agro chemistry (Budoace S. *et al.*, 2004), for esterification of β-keto esters (Sairre M. I. S. *et al.*, 2006) etc.

Due to close values of atomic and ionic radii of Niobium and Tantalum (Shannon R.D., 1976) there is a possibility to obtain mixed oxides of general formula $(Nb_{1-x}Ta_x)_2O_5$, which are mainly used as photocatalysts for water decomposition (Kondo J.N. *et al.*, 2002; Zou Z.G. *et al.*, 2002), catalysis (Yue Y. *et al.*, 2000), biomaterials, nanoporous materials for different applications and materials for optoelectronics (Yang P. *et al.*, 1998).

Niobium and Tantalum alkoxide complexes of common formula $M_2(OR)_{10}$ (M = Nb, Ta; R = Me, Et) are used as catalysts for the carboxylation of alcohols (Dibenedetto A. *et al.*, 2006) and deperoxidation of cyclohexyl hydro peroxide (Saint-Arroman R.P. *et al.*, 2008).

2 Problem definition

There are two important steps in the preparation of functional materials: the first one is synthesis of precursors and the second one the development of materials from them.

Among the Rhenium based catalysts the three the most important ones are Rhenium metal, Rhenium oxides such as ReO_3, Re_2O_7 and of course MTO (methyltrioxorhenium, CH_3ReO_3). The preparation processes for these catalysts normally proceeds under high temperatures and pressures (Räty J. *et al.*, 2000; Okal J., 2005), sometimes starting with harmful substances like $(CH_3)_4Sn$ to obtain MTO (Jain K.R. *et al.*, 2007; Herrmann W.A. *et al.*, 1992).

The biggest limitation of Rhenium (VI) oxide catalyst is that ReO_3 can easily be reduced to inactive ReO_2 and all attempts to oxidize it to regenerate ReO_3 result in the loss of volatile Re_2O_7. Hence it is necessary to create conditions, permitting continuous functioning of these catalysts. It has been shown earlier that incorporation of ReO_3 into the NaY zeolite matrix can produce nanocomposites, where this oxide is more stable to the reducing conditions (Kustov A.L. *et al.*, 2004; Kustov A.L. *et al.*, 2004). The starting material for this catalyst was the oxo methoxide complex $Re_2O_3(OMe)_6$, which was obtained in one step by electrochemical synthesis (Kustov A.L. *et al.*, 2004; Kustov A.L. *et al.*, 2004; Seisenbaeva G.A. *et al.*, 2001). Both Re and Re_2O_7 based catalysts are usually obtained starting from ammonium or Silver perrhenate (Wang L. *et al.*, 2003; Oikawa T. *et al.*, 2004; Mandelli D. *et al.*, 2001; Doledec G. *et al.*, 2000) (*see Fig. 01*).

Unique properties of catalysts based on pentoxides of Ta and Nb, led recently to increased interest to mixed oxides based on both these metals. Several approaches to obtain mixed oxides are described in the literature.

The common preparation method for the multicomponent oxides is usually via conventional solid-state reactions between binary oxides. This method was successfully implemented for the preparation of $(Nb_{1-x}Ta_x)_2O_5$ (Mohanty G.P. *et al.*, 1964), $Bi_3Fe_{0.5}Nb_{1.5}O_9$, (Lufaso M.W. *et al.*, 2007) and many other refractory materials. Unfortunately, the ceramic method requires heat treatment at rather high temperatures and leads to poorly homogeneous materials consisting of larger particles (Camargo E.R. *et al.*, 2002). A number of alternative methods for preparation of multicomponent Nb or Ta oxides have been described. For instance, mixed oxides $SrNb_2O_6$ and $SrTa_2O_6$ were obtained via thoroughly mixing Nb or Ta hydroxides and commercially purchased Strontium hydroxide and prolonged heating at a relatively low temperature (400 °C). The main limitation of this process is that it is multistep and applies the hydrofluoric acid in the preparation of the initial Nb and Ta hydroxides (Muthurajan H. *et al.*, 2008). Other alternative routes such as sol–gel synthesis based on metal-organic precursors, and the citrate method are often considered. Even the citrate method has such limitations as being a multistep and time-consuming procedure (Truijen I. *et al.*, 2007). For instance, $(Nb_{1-x}Ta_x)_2O_5$ solid solutions have been obtained by a neutral templating sol–gel method, using metal pentachlorides as precursors and a block copolymer as a template. According to this method, it is possible to obtain mesoporous $(NbTa)_2O_5$ oxide, which, however, contains chloride impurities (Lee B. *et al.*, 2002; Katou T. *et al.*, 2002). The mesoporous mixed oxides based on Nb and Ta or Mo can also be obtained by thermal decomposition of organic–inorganic precursors with the required ratio of metals in the molecular structure. The syntheses of precursors are complicated and involved several steps, hence providing relatively low yields of the final products (Deligne N. *et al.*, 2007; Bayot D. *et al.*, 2005). Bi- and trimetallic alkoxides complexes can also be used, as precursors of complex oxides that contain required metals at the given ratios. Trimetallic complexes based on Rhenium, Niobium and Tantalum of the following formula $(Nb_{0.5}Ta_{0.5})_4O_2(OMe)_{14}(ReO_4)_2$ and $(Nb_{0.5}Ta_{0.5})_2(OMe)_8(ReO_4)_2$ with the Nb:Ta ratio 1:1 have been described earlier in (Shcheglov P.A. *et al.*, 2002). The synthesis of these complexes was based on the interaction between Re_2O_7 and bimetallic alkoxide of Niobium and Tantalum, $NbTa(OMe)_{10}$ (Hubert-Pfalzgraf L.G. *et al.*, 1975) (*see Fig. 01*). It is possible to obtain these compounds due to isomorphous substitution for Niobium atoms by Tantalum ones, because the ionic radii of Nb and Ta for coordination number 6 are almost the same, 0.64 Å (Shannon R.D., 1976).

Thus, Re, Nb and Ta based materials are useful in almost all spheres of our life. Therefore, the starting point of this research was to develop further the approaches for preparation of precursors based on Re, Nb and Ta, investigate the properties of these complexes and compare them with already known compounds. The final aim was to obtain new functional materials based on these metals via controlled thermal decomposition of the precursors.

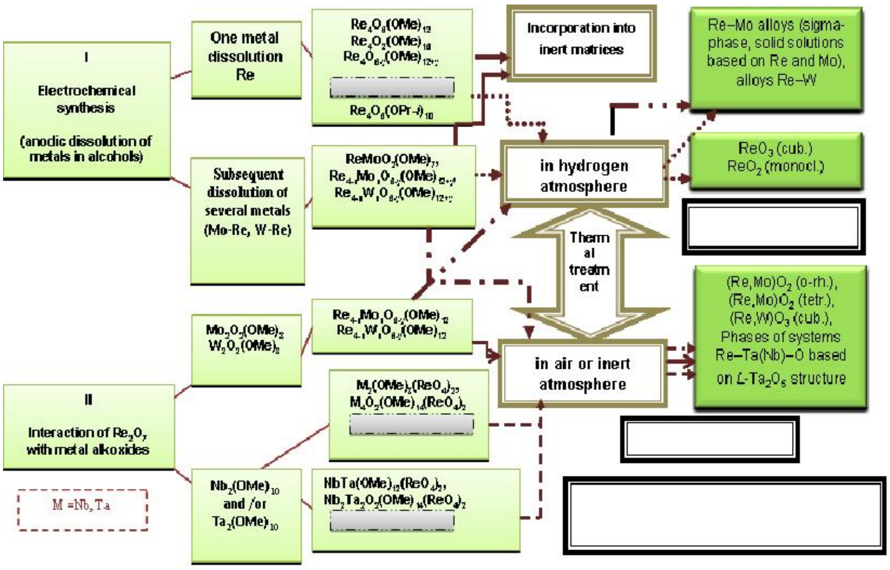


Figure 1. Scheme of preparation of the precursors and related materials.

2.1 Aim

The general aim of our work was to develop new molecular precursor decomposition approaches to Re, Nb and Ta based materials with controlled and, most preferably, organized porosity. We intended also to develop an approach to nanocomposite materials with the active component distributed within a porous matrix through one-step decomposition of a trimetallic molecular precursor.

3 Experimental

Two major approaches to obtain mono-, bi- and trimetallic complexes on the basis of Rhenium, Niobium and Tantalum used in this work were (1) the electrochemical method (for the synthesis of monometallic complexes) and (2) the interaction of Rhenium heptoxide with alkoxo-derivates of Niobium and/or Tantalum. The main advantage of anodic dissolution is a high productivity and simplicity in comparison with the traditional methods based on substitution reactions. The interaction of Re_2O_7 with $M_2(OR)_{10}$ where M = Nb, Ta and R = Me, Et allows to obtain not only the bimetallic but also the trimetallic complexes of the common formula $(M_{1-x}M'_x)_4O_2(OR)_{14}(ReO_4)_2$ (*M = Nb; M' = Ta; R = Me, Et*), where x = 0–1 in a single step, the main advantage of this method.

The thermal decomposition of monometallic ethoxocomplex leads to formation of nanoparticles of metallic Re, in the case of trimetallic methoxocomplexes – formation solid solutions mixed oxides which are related to the block structures of the *H*-modification Nb_2O_5 and the *L*-modification Ta_2O_5. Thermal decomposition in air of these complexes leads to formation porous mixed oxides, with the structures related to the block structure of the *L*-modification of Ta_2O_5.

3.1 Synthesis

Handling of the complexes and all procedures connected with synthesis were carried out in inert (nitrogen) atmosphere in a dry box. Methanol was purified by distillation over magnesium methoxide. Dry ethanol (less than 0.02% H_2O, cat № 100990) was purchased from MERCK and used without further purification. Hexane and toluene was purchased from Aldrich and dehydrated by refluxing over $LiAlH_4$ with subsequent distillation. LiCl for electrochemical experiments has been dried in air at 120 – 150 °C for at least 4 h and then in dynamic vacuum (P~1.3 Pa) at 180 – 200 °C for 1 h. Rhenium heptoxide was purchased from Aldrich with purity 99.9+%. The alkoxides, $Nb_2(OR)_{10}$ and $Ta_2(OR)_{10}$ (R = Me, Et), used in this work as starting materials for the synthesis of bi- and trimetallic complexes, were prepared by anodic oxidation of the corresponding metals in methanol or ethanol respectively and purified according to conventional techniques (Turevskaya E.P. *et al.*, 1995; Turova N. YA. *et al.*, 1996).

$Re_4O_4(OEt)_{12}$ (I) Rhenium was dissolved in ethanol in the electrochemical cell without subdivision into cathode and anode space, supplied with a reflux condenser and water-cooling. LiCl was added as electrolyte. The electrolysis was associated with color changes from colorless to yellow and finally to reddish brown. Crystallization of dark brown plates was observed already during the process of electrochemical synthesis. The crystals were separated by decantation at the end of the process.

$Nb_4O_2(OEt)_{14}(ReO_4)_2$ (II) $Nb_2(OEt)_{10}$ was dissolved in dry toluene. Re_2O_7 was added to the obtained solution and was stirred until complete dissolution. The mixture was quickly heated to 60°C and cooled to the room temperature (r.t.). Then, one sample (**II**) was left for 24 h for crystallization at r.t. (22°C), and the second one (**IIa**) was put into a freezer (-15°C). Yellow crystals have appeared. The solvent was removed by decantation and the crystals were dried *in vacuum* at r.t.

$Ta_4O_2(OEt)_{14}(ReO_4)_2$ (III) A procedure analogous to that for compound **II** was applied, using $Ta_2(OEt)_{10}$ and Re_2O_7. Two samples were crystallized at the two different temperatures: one (**III**) at 22°C and other one (**IIIa**) at (-15°C). Then, the mother liquor was removed by decantation and the practically colorless crystals were dried *in vacuum* at r.t.

$Nb_4O_2(OMe)_{14}(ReO_4)_2$ (IV) and $Ta_4O_2(OMe)_{14}(ReO_4)_2$ (V) Complexes were obtained as described in (Seisenbaeva G.A. *et al.*, 2001) to compare with the complexes (**II**) and (**III**).

$(Nb_{0,7}Ta_{0,3})_4O_2(OMe)_{14}(ReO_4)_2$ (VI) $Nb_2(OMe)_{10}$ and $Ta_2(OMe)_{10}$ were dissolved in 3.5 and 2.5 ml of toluene respectively and then solutions were poured together and mixed in order to achieve Nb:Ta = 0.7:0.3 ratio. Rhenium (VII) heptoxide was added to the obtained solution upon stirring. During dissolution of Re_2O_7 the color of solution changed from light green to pinkish-brown. At the end of the process the mixture was heated to 50°C and the color of the solution became dark brown with red nuance. Then mixture was refluxed during 3–5 min and then cooled to r.t. and left for crystallization. After 24 hours the solution was decanted and the crystalline product (thick needle shaped crystals light lilac in color) was dried *in vacuum* at r.t.

$(Nb_{0,3}Ta_{0,7})_4O_2(OMe)_{14}(ReO_4)_2$ (VII) In order to obtain this complex the same procedure as described above for complex (**VI**) was applied.

$(Nb_{0,5}Ta_{0,5})_4O_2(OMe)_{14}(ReO_4)_2$ (VIII) $(Nb_{0,5}Ta_{0,5})_4O_2(OMe)_{14}(ReO_4)_2$ complex was obtained as described in reference (Shcheglov P.A. *et al.*, 2002) to compare with the complexes (**VI**) and (**VII**).

3.2 Characterization

Several techniques have been used for characterization of the obtained complexes and their derivatives.

The infrared (IR) spectra of Nujol and hexachlorobutadiene mulls were obtained with a Perkin Elmer FT-IR spectrometer Spectrum-100.

Mass-spectra were recorded using JEOL JMS-SX/SX-102A mass-spectrometer applying electron beam ionization (U = 70 eV) with direct probe introduction. The decomposition and sublimation processes in vacuum were studied in glass vessels evacuated by oil pump ($p = 10^{-2}$ mm m.c.). The gaseous products of decomposition were collected in the Schlenk traps cooled with liquid nitrogen. After the decomposition process was accomplished, the system was filled with dry nitrogen and after warming to r.t. a sample of the gas phase from the trap was investigated by GC-MS using Hewlett Packard 5890 Series II gas chromatograph supplied with capillary separating column connected to JEOL JMS-SX/SX102A mass spectrometer.

The results of microanalysis (C, H) were performed by Mikrokemi AB, Uppsala for (**I**) and for complexes (**II - VIII**) on a Heraeus CHN-O-RAPID instrument (standard deviations: C±0.3%, H±0.1%) at the laboratory of Organic Analysis of the Moscow State Academy of Fine Chemical Technology.

^{1}H and ^{13}C NMR spectra were registered for $CHCl_3$ solutions on a Bruker 400 MHz instrument at 300 K.

Thermal analysis (DTA-TGA) was carried out in air at a heating rate 5 °C/min, using Q–1500 D (F, Paulik, J, Paulik, L, Erdey) instrument using 120-300 mg samples (weighing accuracy, ±0.4 mg) at the Department of Chemistry and Technology of Rare Elements of the Moscow State Academy of Fine Chemical Technology. Thermo-gravimetric (TG) studies were carried out with a Perkin-Elmer TGA-7 device and the measurements were performed in nitrogen atmosphere, with the samples of 10–15 mg. The DSC thermograms were recorded with a Perkin-Elmer DSC-2 apparatus at the Department of Physical, Inorganic and Structural Chemistry of the Stockholm University. The DSC equipment was calibrated both on temperature scale and enthalpy by use of metallic Tin.

X-ray powder diffraction (XPD) studies were carried out on a DRON-3M powder diffractometer (CuK$_\alpha$ radiation, scan step of 0.05°-0.1°, counting time of 2-4 s per data point) at the Department of Chemistry and Technology of Rare Elements of the Moscow State Academy of Fine Chemical Technology and by Guinier-Hägg method using CuK$_\alpha$ radiation and silicon as internal standard and with a STADI-P (STOE) diffractometer at the Department of Physical, Inorganic and Structural Chemistry, Stockholm University. The powder patterns were obtained by scanning of the original films using the SCANPI program (Malmros G. *et al.*, 1973; Johansson K.E. *et al.*, 1980).

Transmission electron micrographs and electron diffraction (ED) patterns of the samples were obtained in a JEOL 2000FX-II transmission electron microscope (TEM), equipped with a Link AN-10000 energy dispersive spectrometer (EDS) for microanalysis studies at the Department of Physical, Inorganic and Structural Chemistry, Stockholm University. The metal ratio in the trimetallic precursors and materials derived from them were determined on a HITACHI TM-100 μDex scanning electron microscope (SEM), equipped with a detector for EDAX analysis.

Theoretical analysis of bonding in $Re_4O_4(OEt)_{12}$ was carried out on the basis of molecular orbital diagrams calculated using extended Hückel theory (EHT) level with the use of the CACAO (Mealli C. *et al.*, 1990) program package, applying a model with CH_3-groups as simplified analogs of Et and

^{i}Pr-ones for orbital diagram calculations were made by A.I. Baranov and A. V. Shevelkov.

3.3 X-ray crystallography

For the X-ray single crystal studies the data collection was carried out at r.t. using a Bruker SMART CCD 1 K diffractometer at the Department of Chemistry, SLU and at *T* = 100 K using an Excalibur with sapphire-3 CCD detector (Oxford Diffraction Ltd.) at the Department of Physical, Inorganic and Structural Chemistry, Stockholm University (Mo Kα radiation, graphite-monochromator) for the experimental details see Table 1. The structures were solved by direct methods. Metal atom coordinates were located in the initial solution and all the other non-hydrogen atoms in the subsequent difference Fourier synthesis. All non-hydrogen atoms were refined by full matrix techniques, first in isotropic and then in anisotropic approximation.

Table 1.Crystal data and diffraction experiments.

Sample **Parameter**	**(I)**	**(II)**	**(III)**	**(IIIa)**	**(VI)**	**(VII)**
Space group	P –1	$P2_1/n$			$P2_1/c$	
Crystal system	Triclinic	Monoclinic			Monoclinic	
a, Å	8.359(7)	13.175(5)	12.774(1)	13.227(5)	9.845(6)	10.002(2)
b, Å	10.482(1)	13.532(2)	13.224(9)	13.453(6)	16.001(1)	13.451(4)
c, Å	11.809(2)	14.951(5)	14.855(1)	14.982(7)	12.331(8)	14.233(3)
β, °	72.282(1)	99.967(2)	100.058(8)	100.408(1)	100.860(1)	109.763(6)
V, $Å^3$	938	2625.2(1)	2470.9(4)	2622(2)	1908(2)	1802.1(8)
T, *K*	153	295	295	100	295	295
Number of indepen. reflections (R_{int}),	7090 (0.0492)	2808 (0.0480)	2806 (0.1303)	6864 (0.0827)	2179 (0.0706)	5374 (0.0540)
R_1	0.0377	0.1091	0.0970	0.1239	0.0868	0.0493
wR_2	0.0792	0.1968	0.1807	0.1513	0.1197	0.1001
GoF<F^2>	0.921	1.083	0.990	0.921	0.974	0.925

The coordinates of the hydrogen atoms were calculated geometrically and introduced in the final refinement in isotropic approximation using a riding model. All calculations were performed using SHELXTL-NT program package (*SHELXTL-NT* 1998) on a personal computer. Empirical adsorption correction was made applying the SADABS program.

4 Results and Discussion

4.1 Synthesis and Structure of Precursors

4.1.1 Monometallic Oxoalkoxo Complex – Paper I

The main objective in Paper I was to obtain an individual Rhenium complex, using anodic dissolution of metallic Rhenium in absolute ethanol, a member in the homologous series providing precursors for materials production. We have shown earlier that this process is a productive approach to the alkoxide derivates of Rhenium and it was investigated in such solvents as methanol and isopropanol (Seisenbaeva G.A. et al, 2001; Kessler V.G. *et al.*, 1995; Shcheglov P.A. *et al.*, 2001; Seisenbaeva G.A. *et al.*, 2004). The anodic dissolution of Rhenium in these solvents leads to formation of tetranuclear oxoalkoxide compounds, $Re_4O_{6-x}(OMe)_{12+x}$, containing mainly Re(VI) (Seisenbaeva G.A. et al, 2001, Kessler V.G. *et al.*, 1995) and of $Re_4O_6(O^iPr)_{10}$ (see Fig. 1), were two atoms of Re(V) and two of Re(VI) were present in the same molecule (Seisenbaeva G.A. et al, 2001; Shcheglov P.A. *et al.*, 2001; Seisenbaeva G.A. *et al.*, 2004).

The anodic dissolution of Re in ethanol leads to formation of complexes following formula $Re_4O_4(OEt)_{12}$ which contains planar Re_4-core close to a rhombus in its geometry (*see Fig. 02*). The structure of (**I**) belongs as well as the structure of the oxo isopropoxide $Re_4O_6(O^iPr)_{10}$ to the well known M_4X_{16} core type structure. These structures have a hexagonal dense packing of metal atoms and ligands, one of the most typical for metal alkoxides (Wright D.A. *et al.*, 1968; Turova N. Ya. *et al.*, 2002). It should be mentioned, that for such structures the M – M bonds are typically present. There are several compounds where for such bonding different number of cluster electrons is available. For example, in the structure of compound (**I**)

8 electrons are available for 5 M – M bonds. Two symmetrically equivalent long bonds of 2.63 Å, two other symmetrically equivalent short bonds 2.5358(5) Å and the shorter diagonal of the rhombus which has almost the same lengths 2.5511(5) Å have been observed.

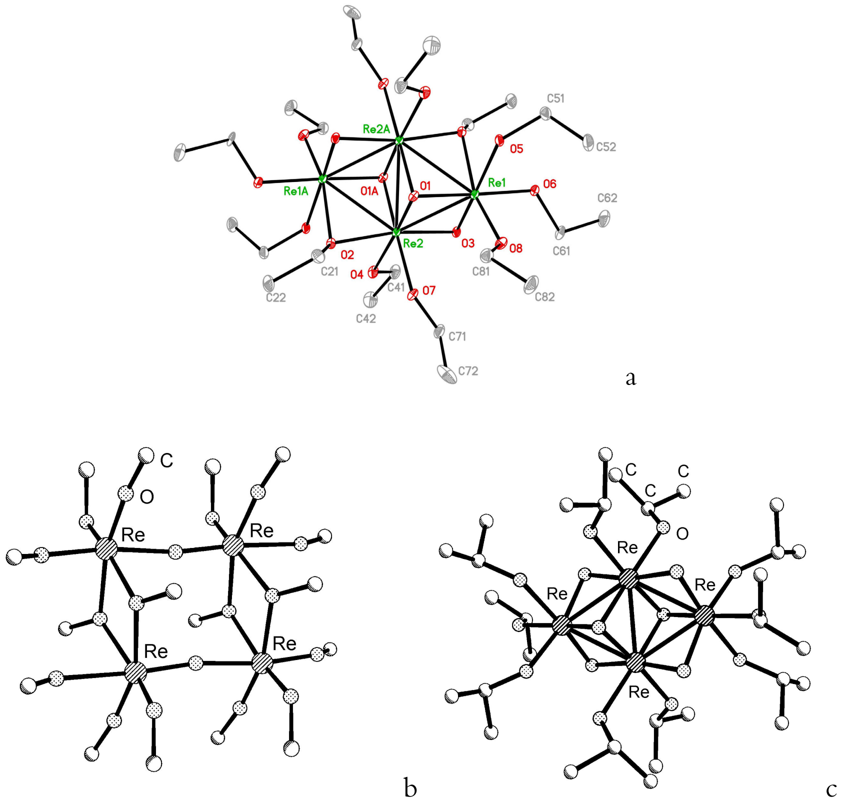


Figure 2. Molecular structures of Rhenium alkoxide homolog's: a – $Re_4O_2(OMe)_{16}$, b – $Re_4O_4(OEt)_{12}$, c – $Re_4O_6(O^iPr)_{10}$.

The same bond arrangement was found also in the structure of $W_4(OEt)_{16}$ (Chisholm M. H. *et al.*, 1981), where the longer side of the rhombus was found to be 2.94 Å, the shorter side being 2.65 Å and the short diagonal – 2.76 Å. In the Rhenium isopropoxide for the same 5 M – M bonds only 6 cluster electrons are available and the bond lengths are almost the same 2.52 – 2.55 Å (Shcheglov P.A. *et al.*, 2001; Seisenbaeva G.A. *et al.*, 2004). The known 4-electron system reveals only two localized M –M bonds, as it has been observed in $Mo_4O_8(O^iPr)_4Py_4$ (Chisholm M. H. *et al.*, 1984).

The *Fig. 02* provides comparison between the structures of all three monometallic compounds. For the methoxide Re(VI)-compound the structure contains only 2 oxo-bridges as each metal center can contain 4 alkoxide ligands in its surrounding, the ethoxocomplex involves already 4 oxo-bridges to compensate the possibility of putting together 2 metals atoms connected with 4 alkoxide ligands and 2 – with only 3 such ligands. The isopropoxide ligand size is already too big and the structure, following the same dense packing as for the $Re_4O_4(OEt)_{12}$, hosts 2 metal atoms with 3 alkoxide ligands and 2 – with only 2 alkoxide ones. From the results of solution and refinement of the structures and IR spectroscopic investigation for all complexes we can confirm that the size of ligands influences the bonds lengths. The increase in the steric tension with incorporation of a bigger alkoxide ligand can even be traced in the increase in the terminal bond lengths on the change in the alkyl group: in the structure of $Re_4O_6(OMe)_{12}$ it is 1,883(7)-1,936(7)Å (Seisenbaeva G.A. *et al.*, 2001), in that of the ethoxide, $Re_4O_4(OEt)_{12}$ (**1**) –1,941(14)-2,13(2)Å, and in that of the isopropoxide, $Re_4O_6(O^iPr)_{10}$, – 1,950(5)-2,148(6)Å (Shcheglov P.A. *et al.*, 2001). The latter is confirmed by comparison of the IR spectra of all complexes (see *Table 2*). The vibrations at 869–970 cm^{-1} can be related to the spectral region of asymmetric Re – O – Re stretching vibrations for all complexes, the bond lengths of which become shorter from $Re_4O_2(OMe)_{16}$ to $Re_4O_6(O^iPr)_{10}$ due to the increased size of the alkoxide ligand. The increasing donor properties of the alkyl radical do not lead thus to any shortening in the metal-oxygen bond lengths.

Table 2. *IR - spectra of Rhenium complexes.*

Compound			**Vibration**
$Re_4O_2(OMe)_{16}$*	**$Re_4O_4(OEt)_{12}$**	**$Re_4O_6(O^iPr)_{10}$***	
1166 m 1123 m 1069 m 1038 st 1021 st	1167 w 1154 w 1082 w 1005 w	1165 m 1140 m 1114 st 1020 m	ν (C - O) + δ (C - H)
	979 w	965 st	ν (Re=O)
	906 st	926 m	ν (Re – O – Re)
966 st br			
870 sh		840 m	ν (C – C)
783 w		814 m	
		755 m	
	769 sh	703 w	δ (C – H)
			ν (Re – $OR_{terminal}$)
597 m		614 m	
564 st		592 m	
544 m		552 w	ν (Re – $OR_{мост}$)
		475 w	ν (Re – $OR_{bridge, terminal}$) +δ (C-C)
431 m	461 m	452 w	

* - literature data (Seisenbaeva G.A. *et al.*, 2001; Shcheglov P.A. *et al.*, 2001)

4.1.2 Bimetallic Oxoalkoxo Complexes – Papers II and III

The aim of Paper II was to obtain new bimetallic complexes on the basis of Nb and Re, Ta and Re using interaction between Rhenium heptoxide and ethoxides of Niobium or Tantalum. The main objective in the Paper III was to investigate and to compare the properties of bimetallic complexes of the common formula $M_4O_2(OR)_{14}(ReO_4)_2$, where M = Nb, Ta and R = Me, Et. Bimetallic oxomethoxo complexes based on Re and Nb or Ta of the following formulae $M_4O_2(OMe)_{14}(ReO_4)_2$ and $M_2(OMe)_8(ReO_4)_2$ (M = Nb, Ta) (Seisenbaeva G.A. *et al.*, 2001; Shcheglov P.A. *et al.*, 2002; Seisenbaeva G.A. *et al.*, 2001) were described previously. The methoxide compounds are demonstrating rather low solubility, which limits their applicability for preparation of coatings. Therefore the purpose of this work was to obtain new compounds having good solubility in non-polar solvents, which could be used for preparation of catalysts.

The bimetallic complexes (**II**) and (**III**) have been prepared via interaction of Rhenium heptoxide, Re_2O_7, and Niobium and Tantalum alkoxides, $M^{v}_{2}(OR)_{10}$ (R = Me, Et), in hydrocarbons. Samples which were crystallized at room temperature 22°C and low temperature -15°C for both compounds have been taken. The structures of these compounds were determined by X-ray single crystal diffraction (see *Table 01*). For complex **III** two different modifications were discovered: one that crystallized at room temperature (sample **III**) and one– at low temperature (**IIIa)** (see Table 1 in Paper II). Their molecular structures (see *Fig. 03*) are based on a tetranuclear $M_4(\mu\text{-}O)_2(\mu\text{-}OR)_4X_{12}$ core, X = OR, ReO_4, with rectangular planar M_4-arrangement (M = Nb, Ta), composed of two pairs of edge-sharing octahedra, joined via two almost linear oxo-bridges. The perrhenate ligands are attached in a centrosymmetric manner to the two opposite corners of the rectangle (see *Fig. 03*).

Two different modifications of $Ta_4O_2(OEt)_{14}(ReO_4)_2$, which were crystallized at the different temperatures, differ considerably in the values of unit cells parameters and density of the samples. For the sample **IIIa** the density is much higher than for the sample **III**, which is connected with temperature of crystallization. It is to be noted that in case of methoxo complexes the decrease in crystallization temperature led to formation of new non-oxo methoxocomplexes of the common formula $M_2(OMe)_8(ReO_4)_2$, where M = Nb, Ta (Shcheglov P.A. *et al.*, 2002; Seisenbaeva G.A. *et al.*, 2001). This difference between methoxides and ethoxides is caused evidently by easier oxidation of ethanol resulting in release of water and formation of oxo-species. Thus, we can conclude that the temperature of crystallization influences mostly the unit cell parameters; density and volume of the unit cell, but not so much the bond lengths (see Tables 1, 2 in Paper II).

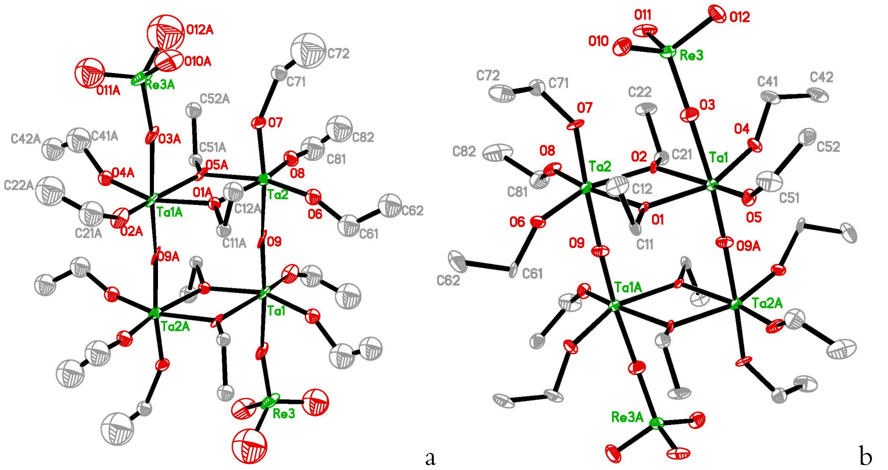


Figure 3. Molecular structures of the III and IIIa samples of Ta$_4$O$_2$(OEt)$_{14}$(ReO$_4$)$_2$: a – sample crystallized at 22 °C; b – sample crystallized at – 15 °C.

The temperature of crystallization also substantially affects the perrhenate group geometry. For the samples **II**, **III**, **IV** and **V** it was observed that the perrhenate group had ideal tetrahedral geometry (see Table 2 in Paper III) in contrast to sample **IIIa** (crystallized at low temperature), where the same group was distorted due to interaction with an ethoxo-group in the packing. The size of alkoxide ligand is influencing the position of the perrhenate group. Comparing the ReM1M2 and ReM1M(2A) angles (see *Fig. 03* and Table 3 in Paper III) for all complexes it was found that in the methoxocomplexes **IV** and **V**, the ReO$_4^-$ group is turned toward the terminal methoxo group due to the smaller volume of a free space in the crystal lattice of these complexes. For ethoxo complexes **II**, **III** and **IIIa** the perrhenate group is turned toward the bridging ethoxo group. It should be mentioned, that ReM1M(2A) angles decrease from the sample **II** to sample **V** and ReM1M2 angles increase in the same series, which is, obviously, connected with the increasing size of the alkoxide ligand.

The increasing size of the ligand is also influencing the bond lengths in all the complexes, which is confirmed by the IR – spectra and by the results of solution and refinement of the structures (see Figs. 2, 3 in Paper III and *Table 3*). The bond lengths increase in the following order:

r(Re-O)term < r(Re-O)μ < r(M-OR)term < r(M-O)μ < r(M-OR)μ < r(M-O-Re)μ.

Table 3. *IR – spectra of bimetallic complexes of common formula* $M_4O_2(OR)_{14}(ReO_4)_2$ *(M = Nb or Ta, R = Me, Et)*

Compound	IV	II	V	III	Vibration
IR–spectra recorded in Nujol		1277 s w			
	1146 s w		1151 s	1132 sh	
	1097 s w	1099 m w	1114 m	1108 m w	ν (C - O) + δ (C - H)
	1062 sh	1068 m		1076 m	
		1020 sh		1018 m w	
	930 st	932 st	996 m w	936 st	ν (Re=O)
	889 sh	892 sh	933 st	892 sh	ν (M–O–M)
	807 m w	878 m	901 sh	876 m	
	768 sh				
		814 st	810 st w	810 st	ν (C – C)
	722 m	722 s	772 m	772 s	δ (C – H)
	571 m	599 s	569 sh	527 s	ν ($M–OR_{term}$)
	526 m	536 m w	507 st w	479 s	ν ($M–OR_{bridg}$)
		478 s w		478 s w	ν ($Re – OR_{bridg, term}$)+δ (C-C)
IR–spectra recorded in HCB		1915 s w	1915 s	1917 s	
	1917 s				
	1792 s				
	1634 s	1634 sh	1634 s	1634 s	
	1611 st	1611 st	1611 st	1611 st	
	1564 st	1564 st	1564 st	1564 st	ν (C - C) + δ (O – H)
		1470 m		1473 sh	
			1455 m w	1445 m	
	1452 st w	1379 m	1399 s	1407 sh	
		1356 sh	1379 s	1383 st	
		1276 s		1358 sh	

Thus, the ligand size and crystallization temperature affect the crystallographic parameters and the position and geometry of perrhenate group, and also the bond lengths in the bimetallic complexes of common formula $M_4O_2(OR)_{14}(ReO_4)_2$, where M = Nb or Ta, R = Me, Et. In addition, it was established, that the ethoxide complexes in contrast to methoxide ones have good solubility in hexane, toluene and other non-polar solvents, which makes them attractive precursors of complex oxide coatings for catalytic applications. The decisive role in solubility is played, evidently, by the size of the alkoxide ligand.

4.1.3 Trimetallic Oxoalkoxo Complexes – Paper IV

The aim of Paper IV was to obtain new trimetallic oxoalkoxo complexes of the common formula $(Nb_xTa_{x-1})_4O_2(OMe)_{14}(ReO_4)_2$, where x = 0.3, 0.7, which can be used for preparation of complex porous oxide materials. Previously, we have described that isomorphous replacement of Niobium by Tantalum atoms in the structure allows to obtain trimetallic complexes of following compositions $(Nb_{0.5}Ta_{0.5})_4O_2(OMe)_{14}(ReO_4)_2$ and $NbTa(OMe)_8(ReO_4)_2$ (Shcheglov P.A. *et al.*, 2002).

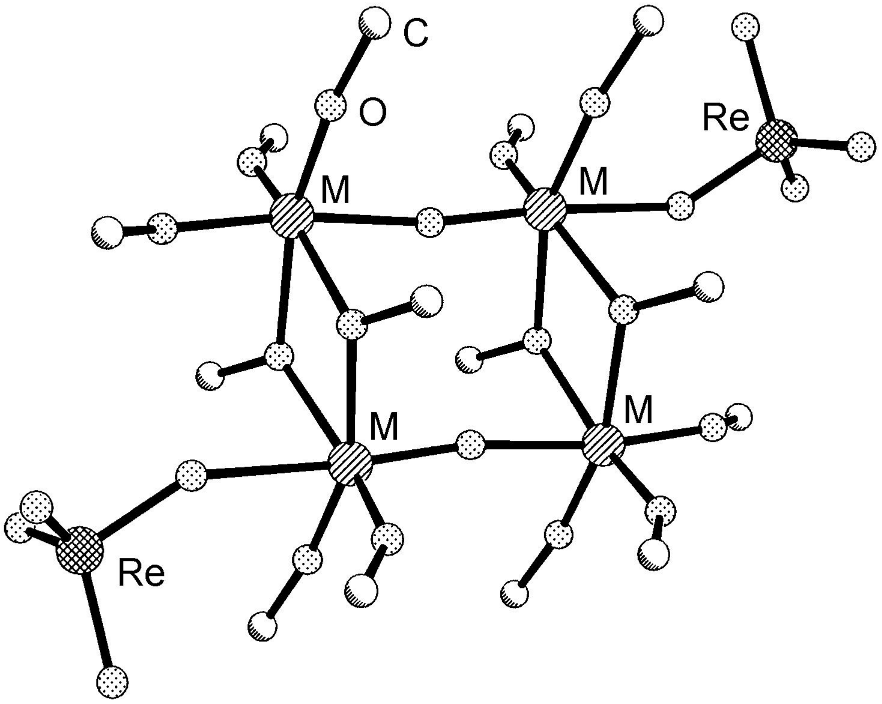


Figure 4. The molecular structure of trimetallic complexes of common formula $(Nb_xTa_{x-1})_4O_2(OMe)_{14}(ReO_4)_2$, where x = 0.3, 0.5, 0.7.

In order to obtain new complexes $(Nb_{0.7}Ta_{0.3})_4O_2(OMe)_{14}(ReO_4)_2$ (**VI**) and $(Nb_{0.3}Ta_{0.7})_4O_2(OMe)_{14}(ReO_4)_2$ (**VII**) the same method as for $(Nb_{0.5}Ta_{0.5})_4O_2(OMe)_{14}(ReO_4)_2$ complex (**VIII**) was applied, based on the consequential interaction Re_2O_7 with methoxides $Nb_2(OMe)_{10}$ and $Ta_2(OMe)_{10}$ in toluene. The molecular structure of (**VI**) and (**VII**) are analogous to the structures of (**II**), (**III**), (**IV**), (**V**) and (**VIII**), and is shown in *Fig 04.* The results of solution and refinement of the structure show significant distinctions between the unit cell parameters of the samples (see

Table 01 in Paper IV). As it can be seen from the results, the unit cell parameters and related characteristics, i.e. density and volume of unit cell, are depending on ratio between Niobium and Tantalum in the complexes. It was found earlier that the distribution of metals for the (**VIII**) complex in the crystallographic positions in the structure is uneven. The atoms of Niobium are mainly placed in the M1 "oxo"-position (see *Fig. 04*), i.e. the position in which the atom of metal is connected with a perrhenate [ReO_4^-] group through an oxo-bridge, and the atoms of Tantalum are mainly situated in the M2 "alkoxo"-position. Occupation of the first position composes approximately 70% Nb + 30% Ta, while the latter one 30% Nb + 70% Ta (Shcheglov P.A. *et al.*, 2002). This trend in distribution of metal atoms is preserved for the trimetallic oxoalkoxo complex with ratio between Nb and Ta 70:30 according to the structure refinement statistics. For the $(Nb_{0,3}Ta_{0,7})_4O_2(OMe)_{14}(ReO_4)_2$ complex this distribution is not traced evidently because of increased Tantalum content in the compound. It should thus be concluded that it is the increased Niobium content (Nb:Ta = 1:1 and higher) that favours the uneven distribution of metals cations. The contents of Niobium and Tantalum in the composition of trimetallic complexes influences the parameters and the volume of unit cell, which vary with the increase in the Tantalum content and decrease in the Niobium content in the oxomethoxo complexes. The decreasing of volume of unit cell in the series from $(Nb_{0,7}Ta_{0,3})_4O_2(OMe)_{14}(ReO_4)_2$ to $(Nb_{0,3}Ta_{0,7})_4O_2(OMe)_{14}(ReO_4)_2$ is observed from the results of solution and refinement of the structure (see Table 01 in Paper IV), and connected with prevalence of the statistic distribution of metals in occupation of the crystallographic positions in the structure (**VI**).

IR – spectra recorded in Nujol are in agreement with the molecular structure. For all complexes the absorption bands were found in the same region. This confirms that all complexes have the same structure (see Table 03 - IV). Because the Nujol peaks appear in the same region 1300 – 1700 cm^{-1} as the stretching and bending vibrations of C–C, C=C, O–H for the all samples, the spectra were recorded also in HCB. The peaks of methoxo groups are clearly seen in these spectra for all samples (see *Table 4*). It should be mentioned, that the bond lengths for all samples are approximately the same, only for the complex (**VIII**) a slight shortening of M – O bonds is observed connected, probably, with the ratio between Nb and Ta, and also less disorder in the structure (see Table 2 in Paper IV).

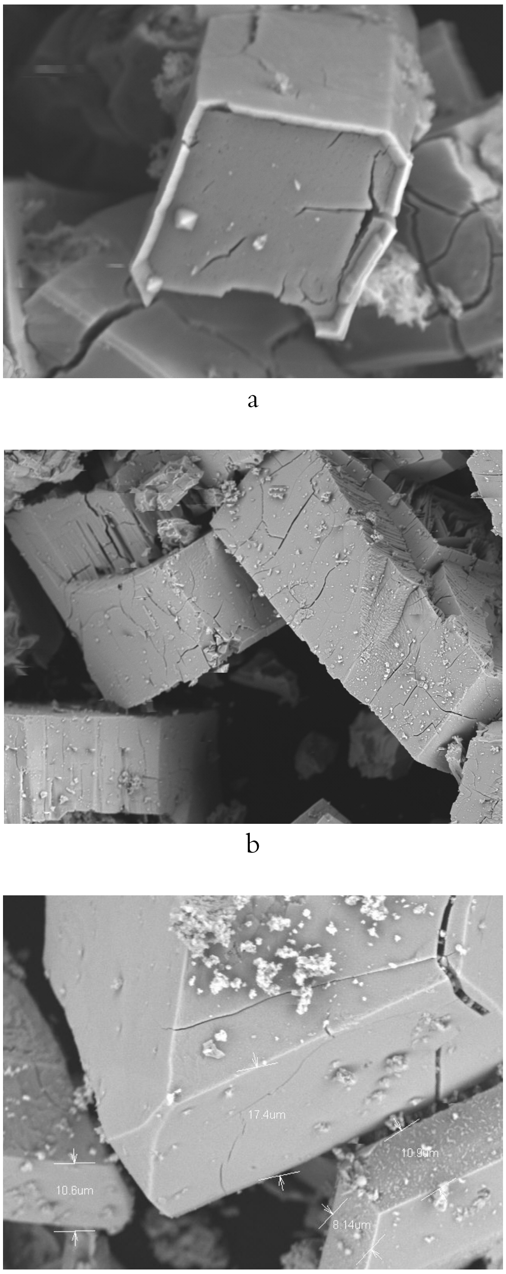
Table 4. *IR – spectra of* $(Nb_xTa_{x-1})_4O_2(OMe)_{14}(ReO_4)_2$ ($x = 0.3, 0.5, 0.7$)

Compound	VI	VIII	VII	Vibration
IR – spectra recorded in Nujol			1160 sh	ν (C - O) +
	1109 st w	1117 m w	1106 m w	δ (C - H)
	995 m w	994 s w	995 m w	
			941 m	ν (Re=O)
	930 st	929 m	927 s	ν (M – O – M)
	890 s w	893 s w	897 s	
	805 st w	807 m w	807 m w	
	721 s	720 s	720 s	δ (C – H)
	567 m w	564 s w	560 s w	ν (M – OR_{term})
	516 m w	512 s w	533 sh	ν (M – OR_{bridg})
			496 s w	
IR- spectra recorded in HCB	1633 s	1631 s	1628 w	ν (C - C) + δ (O – H)
	1607 m	1604 m	1610 m	
	1561 st	1561 st	1561 st	

For identification and characterization of the bulk samples of trimetallic species (**VI)** and (**VII**), the XRD and SEM-EDS analysis of powder of the initial complexes was carried out (see Figs. 2-4 in Paper IV).

The powder patterns (see Figs. 2 and 3 in Paper IV) of the initial trimetallic complexes (**VI**), (**VII**) display rather narrow peaks indicating high crystallinity of the samples. All reflections can be indexed in the unit-cell parameters characteristic of the complexes, which confirms the phase purity of the obtained products.

The SEM study of the powder of initial complexes (**VI**), (**VII**) and (**VIII**) showed that all samples have well formed crystalline appearance (see *Fig. 05*). Different shapes and sizes of crystals for all complexes can be seen in the SEM micrographs caused supposedly by different crystallization preferences revealed for different compositions.



a

b

c

Figure 5. The SEM micrographs a – **VI,** b – **VIII**, c – **VII**.

The EDS analysis shows (see Table 4 in Paper IV) that the crystallization of all complexes from solutions proceeded unevenly, probably because of the partial formation of the individual $(Nb_{0.5}Ta_{0.5})_2(OMe)_8(ReO_4)_2$ as impurity (Shcheglov P.A. *et al.*, 2002). Some crystals have relatively higher and some—lower Nb:Ta ratio compared with the average values imposed by the conditions of synthesis. The average ratios between Nb, Ta and Re were approximately the same for the samples of (**VI**), (**VII**) and (**VIII**) and for the isolated single crystals.

Thus, the results of SEM and powder XRD analyses show that it is possible to synthesize trimetallic complexes on the base of Rhenium, Niobium and Tantalum with a given ratio.

4.2 Preparation of Metal and Complex Oxide Materials

The comparably low temperatures and one-step thermal decomposition in different atmospheres makes this method useful to obtain nanoparticle metal aggregates of Re from the complex (**I**) and mesoporous mixed oxides based on Nb and Ta from the complexes (**VI**) – (**VIII**).

4.2.1 Preparation of Rhenium Metal – Paper I

In Paper I, $Re_4O_4(OEt)_{12}$ was used as precursor to obtain nanoparticles of Rhenium metal. X-ray powder analysis shows that complex (**I**) is not stable in the ambient atmosphere. X-ray powder pattern of $Re_4O_4(OEt)_{12}$, taken from the fresh sample **I,** indicates difference in peaks positions and intensities from the pattern which was generated by ATOMS software (ATOMS for Windows 2006) based on the parameters from the single crystal X-ray study of (**I**). Therefore, a pattern of a hypothetical structure model $Re_4O_6(OEt)_{10}$ related to $Re_4O_6(O^iPr)_{10}$ (Seisenbaeva G.A. *et al.*, 2004) (see *Fig. 06*) was calculated. From the comparison of the powder patterns it can be concluded that complex (**I**) is easily oxidized to $Re_4O_6(OEt)_{10}$, in analogy to the earlier studied isopropoxide derivative. It should also be noted that the Re_4-cluster core is not destroyed in the ambient atmosphere.

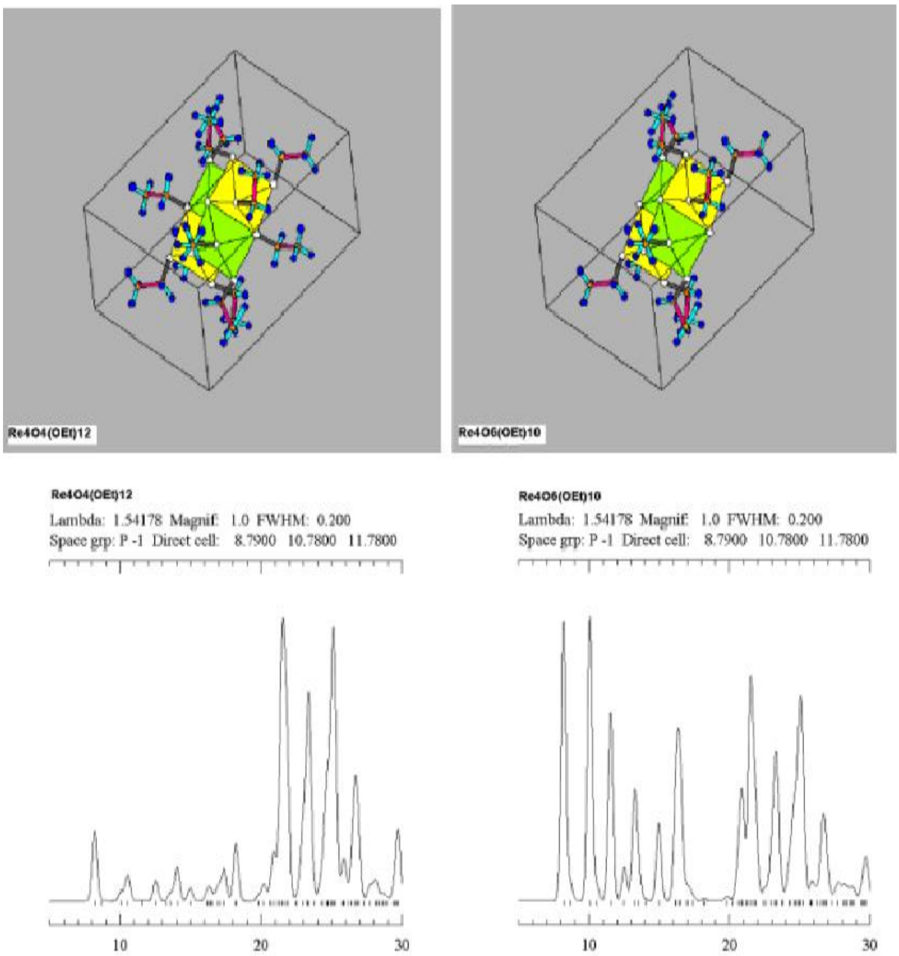


Figure 6. The molecules of $Re_4O_4(OEt)_{12}$ and $Re_4O_6(OEt)_{10}$ in the unit cell and the resulting theoretical X-ray patterns, generated by ATOMS software (ATOMS for Windows 2006)

The complex (**I**) was annealed at three different temperatures in N_2 atmosphere. The first sample (at 250 °C) reacted spontaneously with air forming a white smoke. The second sample (heated up to 300 °C) was black in color and was amorphous. The last sample (450 °C) showed metallic color and seemed to be stable to air. After TG analysis of the latter sample was investigated by XPD analysis and showed the formation of Re metal particles according to ICDD data (№ 05-0702) for Re metal. TEM studies of the products showed that the product obtained at 450 °C consisted of strongly agglomerated nanocrystals approximately 3 nm in size (see *Fig. 07*). EDS analysis in TEM confirmed that the sample consisted of Re.

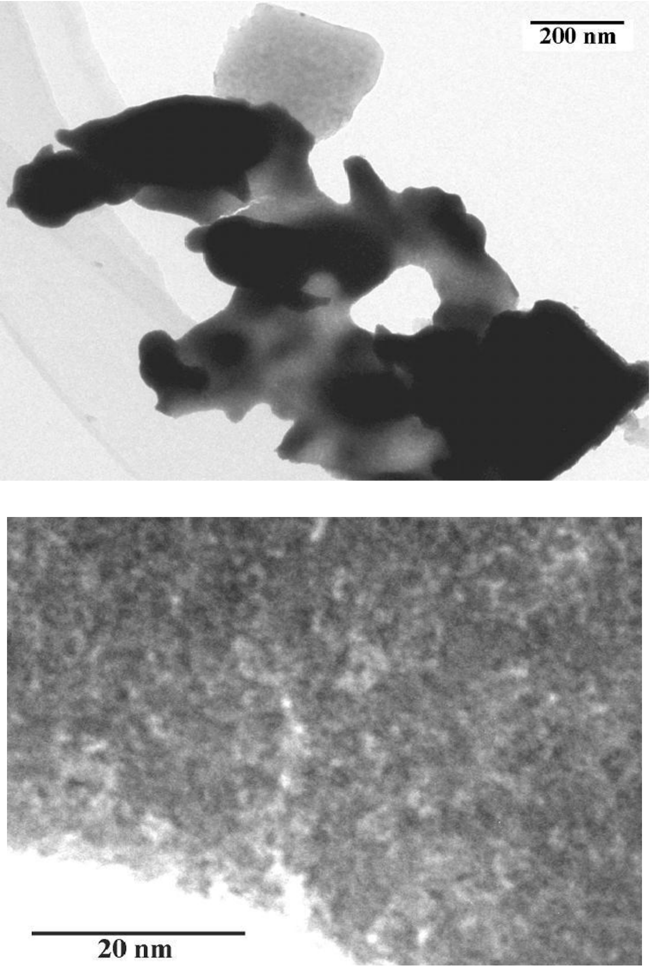


Figure 7. TEM micrographs of Rhenium oxoethoxide heated at 450 °C, in N_2.

Thus it has been established that the thermal decomposition of $Re_4O_4(OEt)_{12}$ proceeds in a principally different way compared to $Re_4O_6(OMe)_{12}$ and $Re_4O_6(O^iPr)_{10}$. For the last two complexes ReO_3 was the only product of the first step in decomposition, and it transformed further into ReO_2 stable to at least 800 °C (Kustov A. L. *et al.*, 2004; Kustov A. L. *et al.*, 2004). Rhenium metal could be obtained from methoxide or isopropoxide only using hydrogen gas as reductive agent at the temperature of 380 °C (see *Fig. 08*). Transformation into metal on heating in the inert atmosphere, without introduction of any reductive agent, makes Rhenium ethoxide, $Re_4O_4(OEt)_{12}$, an attractive precursor of Rhenium nanopowder material for deposition into mesoporous templates such as Al_2O_3, Nb_2O_5 or Ta_2O_5.

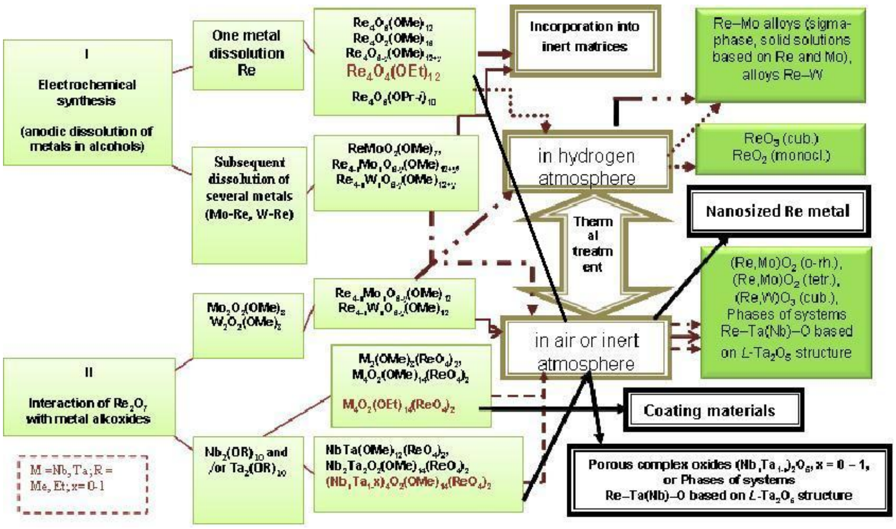


Figure 8. Scheme of preparation precursors and materials based on it.

4.2.2 Preparation of Oxide Materials – Paper IV

The preparation of oxide materials from the trimetallic oxomethoxo complexes based on Nb, Ta and Re with the ratios between Niobium and Tantalum 0.3, 0.5, 0.7 can be successfully achieved as presented in the Paper IV.

Complexes (**VI**), (**VII**) and (**VIII**) were subjected to thermal decomposition in air on heating up to 1000 °C with the heating rate of 5 °C/min. TGA revealed two steps in decomposition. The values of weight loss after the first step are close to the theoretical values, corresponding to the products presented in Table 5 in Paper IV. The second step, occurring on heating above 500 °C, is connected with the evolution of Rhenium heptoxide (Re_2O_7(g)) into the gas phase.

After the thermal decomposition in air, the products of heat treatment were investigated using powder XRD and SEM-EDS. The samples of the decomposition products reveal narrow and very closely situated reflections, indicating high crystallinity (see Fig. 5 in Paper IV). According to the results of powder XRD analysis for the investigated compositions $(Nb_{1-x}Ta_x)_2O_5$, where x = 0.3, 0.5, 0.7, we can conclude that isomorphous replacement of Nb with Ta increases the temperature stability domain of the of L(γ)-modification-related M_2O_5 phase up to 1000 °C. These data confirm the formation of solid solutions of Niobium and Tantalum oxides $(Nb_{1-x}Ta_x)_2O_5$ on the decomposition of trimetallic complexes $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$, where x = 0.3, 0.5, 0.7.

The SEM investigation shows that all the products of decomposition have a crystalline, semi-ordered porous structure (see *Fig. 09*) with size of the pores 100–250 nm. Based on the SEM micrographs of initial complexes and their products of decomposition (see *Figs. 05* and *09*) we can confirm that crystals save the form and show a high stability to high temperature treatment (1000 °C). The EDS analysis shows that the ratios between Nb and Ta is changed for the samples (**VI**) and (**VII**) which is probably connected with the higher volatility of Niobium alkoxide derivatives compared to Tantalum ones as confirmed by the mass-spectral investigation. An analogous relation in relative volatility of Niobium and Tantalum components in a complex has earlier been observed in the classic work of L.G. Hubert-Pfalzgraf on bimetallic Niobium – Tantalum alkoxides (Hubert-Pfalzgraf L.G. *et al.*, 1978). Hence, we can note that the thermal decomposition of trimetallic oxomethoxo complexes (VI), (VII) and (VIII) opened an approach to formation of solid solutions of complex porous oxides based on *L* – modification of Ta_2O_5 of common formula $(Nb_{1-x}Ta_x)_2O_5$, where $x = 0.3, 0.5, 0.7$.

For the complexes (**VI**) – (**VIII**) the thermal decomposition was also carried out in N_2. The results of TG analysis show that all samples contained traces of Rhenium, which is confirmed by assignment of indices in the XPD patterns. The results of unit cell parameters calculation (see Table 8 in the Paper IV), based only on peaks with strong intensity, showed for $(Nb_{0,7}Ta_{0,3})_4O_2(OMe)_{14}(ReO_4)_2$ that the sample contained a phase related to monoclinic *H* - Nb_2O_5 modification. The patterns obtained for the samples derived from complexes (**VII**) and (**VIII**) contained a phase related to the *L*-modification of Ta_2O_5 (see *Fig. 08*). It is connected, most likely, with the fact that enters more Niobium than Tantalum into the structure of the complex (**VI**). Hence, changing the ratio between Niobium and Tantalum it is possible to control the phase composition in relation to modifications related to the known structure types of Nb_2O_5 or Ta_2O_5.

We can note that volumes of the unit cell for Nb:Ta = 50:50 and the pure pentoxide of Tantalum Ta_2O_5 are practically identical, while for the intermediate Nb:Ta compositions = 30:70 the cell volumes are essentially bigger. We suggest that intermediate compositions are characterized by more disordered arrangement of cations.

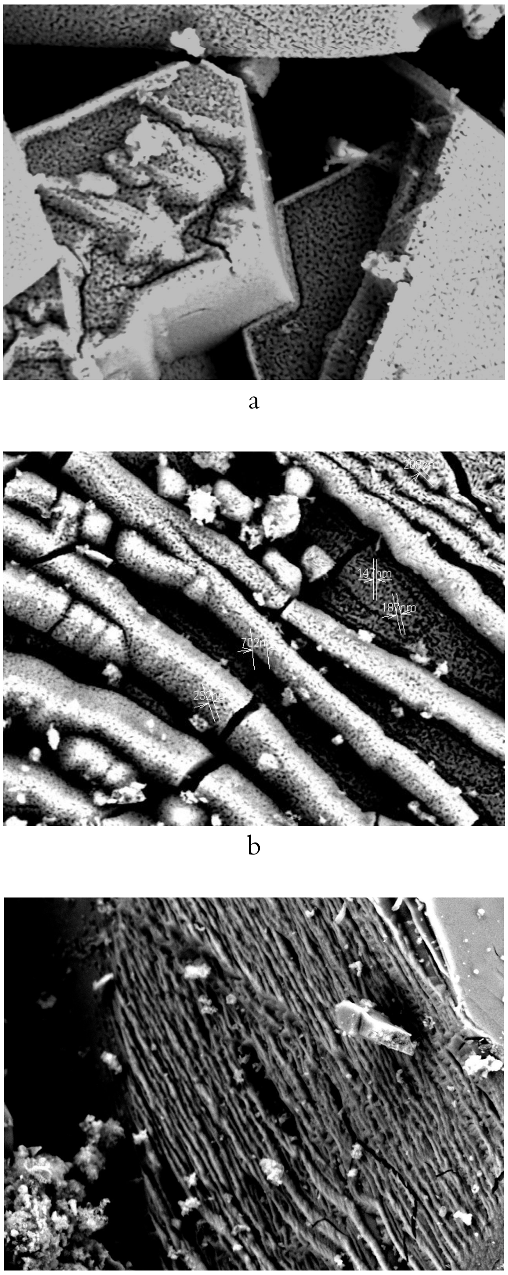


Figure 9. The SEM micrographs the products of decomposition in air: a – $(Nb_{0,7}Ta_{0,3})_4O_2(OMe)_{14}(ReO_4)_2$; b – $(Nb_{0,5}Ta_{0,5})_4O_2(OMe)_{14}(ReO_4)_2$; c – $(Nb_{0,3}Ta_{0,7})_4O_2(OMe)_{14}(ReO_4)_2$.

Thus, the thermal decomposition in air of all the studied complexes $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$ ($x = 0.3, 0.5, 0.7$) leads to solid solutions related to the block structure of *L*-modification of Ta_2O_5 at the temperatures < 1000 °C with semi-ordered macro porous structures, where the size of pores lies in the range 100-250 nm. The thermal decomposition in dry nitrogen provides solid solutions related to the block structures of the *H*-modification of Nb_2O_5 for the Niobium-rich precursors and the *L*-modification of Ta_2O_5 for Ta:Nb > 1:1 at the temperature < 1000 °C (see *Fig. 08*).

5 Conclusions

In our work we used two major synthetic approaches, the electrochemical synthesis and the reaction of interaction between heptoxide of Rhenium and alkoxide complexes of Niobium and Tantalum. Both approaches were successfully used for preparation of new mono-, bi- and trimetallic complexes and materials based on the Re, Nb and Ta, which are attractive for application as catalysts for different organic reactions.

The electrochemical synthesis based on the anodic dissolution of Rhenium metal in absolute EtOH turned out to be successful for the synthesis of $Re_4O_4(OEt)_{12}$ complex with the yields of the crystalline product about 70-80 % (see *Fig. 08*).

The interaction of Re_2O_7 and ethoxide complexes with the common formula $M_2(OEt)_{10}$ (M=Nb, Ta) led successfully to the preparation of bimetallic $Nb_4O_2(OEt)_{14}(ReO_4)_2$ and $Ta_4O_2(OEt)_{14}(ReO_4)_2$ oxoethoxo complexes with as high yield of the bulk products as 83 and 86 % respectively (see *Fig. 08*).

Due to isomorphous substitution for Niobium atoms by Tantalum ones it is possible to obtain by addition of Re_2O_7 the trimetallic oxomethoxo complexes with the common formula $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$, where x = 0.3, 0.5, 0.7 with high yields (91, 92, 91% respectively). The distribution of Nb and Ta is even at Nb:Ta = 1:1 but is a subject of considerable variation for the Nb- and Ta-rich samples, respectively (see *Fig. 08*).

Established that, on the structures of precursors and properties of obtaining from them materials influence the increasing of ligand in the case of $Re_4O_4(OEt)_{12}$ and bimetallic complexes of common formula $M_4O_2(OR)_{14}(ReO_4)_2$ (M = Nb, Ta; R = Me, Et) and ratio between Nb and Ta in the trimetallic complexes.

Nanosized particles, 3 nm, of metallic Rhenium were successfully obtained after thermal decomposition of $Re_4O_4(OEt)_{12}$ in dry N_2 atmosphere at low temperatures (see *Fig. 08*).

The thermal decomposition in air of all the studied complexes $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$ (x = 0.3, 0.5, 0.7) leads to solid solutions with the structures related to the block structure of the *L*-modification of Ta_2O_5 at the temperatures < 1000°C with semi-ordered macro porous structures, where the size of pores lies in the range 100-250 nm. The thermal decomposition in dry nitrogen provides solid solutions with the structures related to block structure of the *H*-modification of Nb_2O_5 for the Niobium-rich precursors and the *L*-modification of Ta_2O_5 for Ta:Nb > 1:1 at the temperature < 1000°C (see *Fig. 08*).

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