Heteroligand alkoxides of rhenium containing O-Et and O-iPr ligands.

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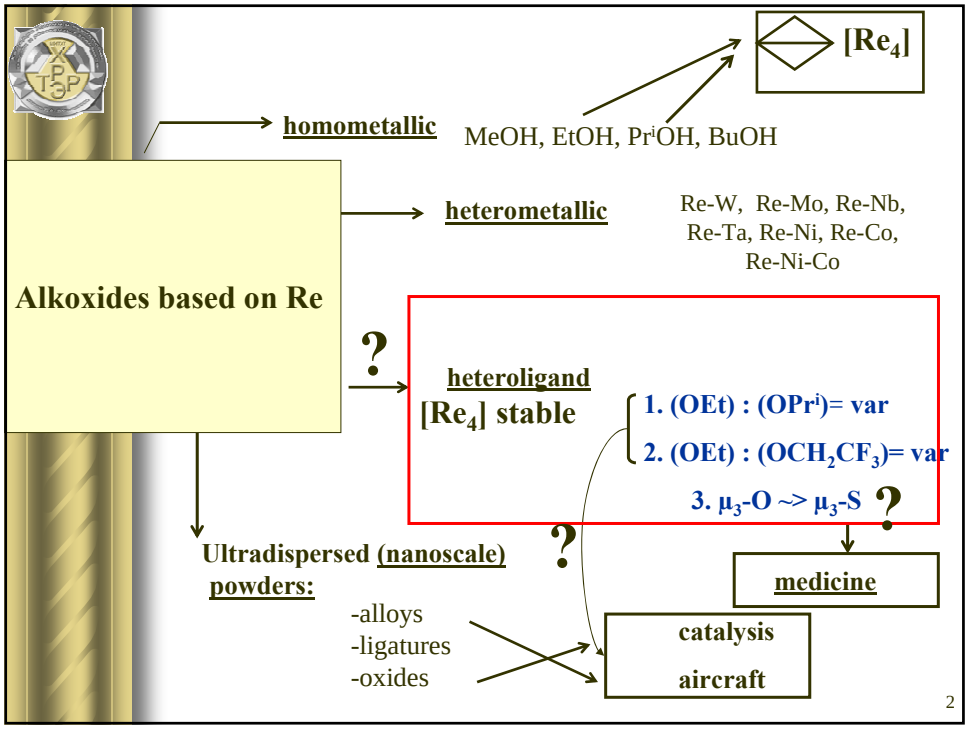
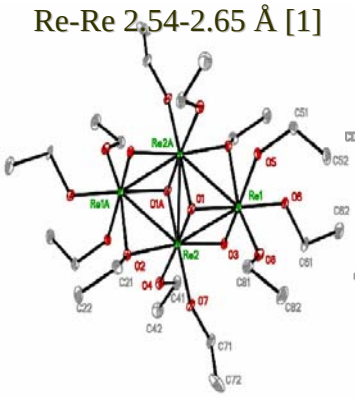
Moscow ISTR2011

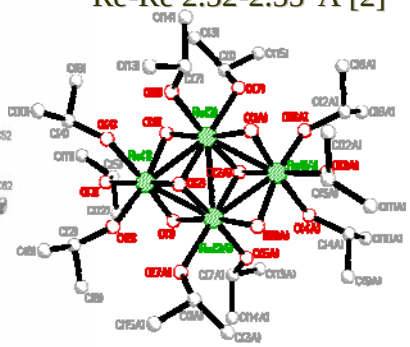


Structures containing cluster Re_4

$Re_4O_4(OEt)_{12}$ Re-Re 2.54-2.65 Å [1]



$Re_4O_6(OPr^i)_{10}$ Re-Re 2.52-2.55 Å [2]



[1] Olesya A. Nikonova, Kjell Jansson, Vadim Kessler, Margareta Sundberg, Alexei I. Baranov, Andrei V. Shevelkov, Pavel A. Shcheglov, Dmitrii V. Drobot and Gulaim A. Seisenbaeva . Electrochemical synthesis, structural characterization and decomposition of rhenium oxoethoxide, $Re_4O_4(OEt)_{12}$. Ligand influence on the structure and bonding in the tetranuclear planar rhenium alkoxide clusters. Inorg. Chem.47, 1295-1300.

[2] Sheglov P.A. Mono-, Bi- and trimetallic oxo- alkoxoderivatives of rhenium (sinthesis, properties and application) // Diss. Cand. Chem. science. MIFCT. Moscow. 2002.

MAIN AIMS

The main aims of this investigation are the quantum-chemical foundation the ligand nature influence on the stability of alkoxides of rhenium, the synthesis of heteroligand complexes of rhenium and study of their properties.

Computer Aided Composition of Atomic Orbitals (C.A.C.A.O.)

A Package for Molecular Orbital Analysis

[PC Beta-Version 5.0 , 1998]

Carlo Mealli u Davide M. Proserpio

With major contribution of

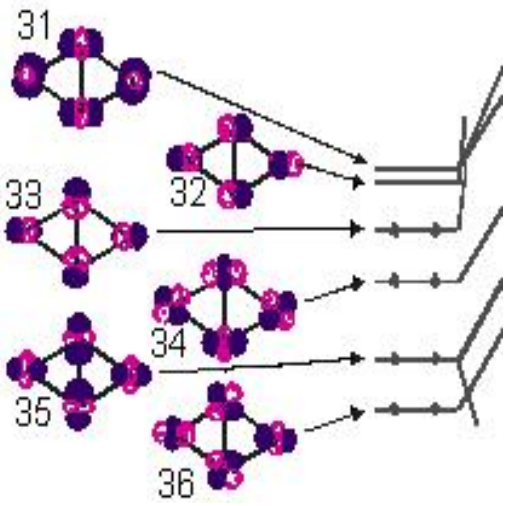
Andrea Ienko.

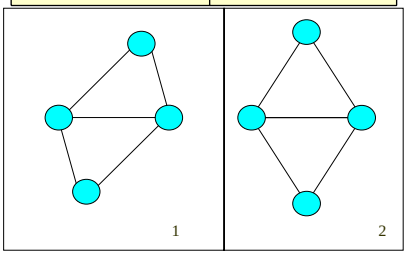
Package Technical Information

- ***Method – Extended Method of Hukkel.***
  - ***Molecules geometry is approximate to the real.***
  - ***Usage of radicals –CH3 and –CF3 instead of –C2H5 and –CH2CF3 (simplify analogues)***
- ***The findings can not use in the capasity of referenced data and employed for the comparison analysis in this program.***

Cluster Re_4

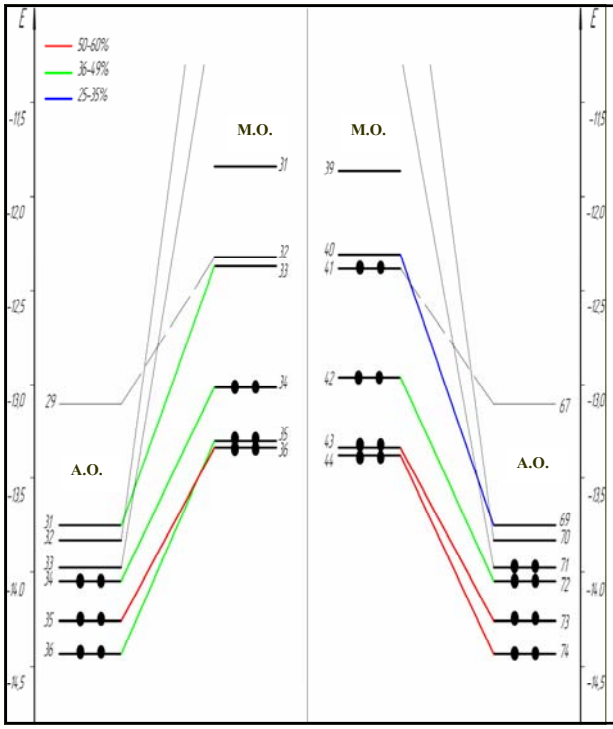
№1	№2
$Re_4O_4(OEt)_{12}$	$Re_4O_6(OPr^i)_{10}$
Re (V)	Re (V, VI)
$[Re4]^{20+}$	$[Re4]^{22+}$
e=8	e=6
C2h	D2h



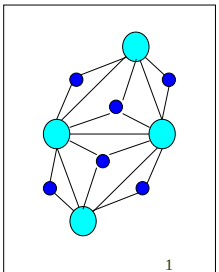


- Re

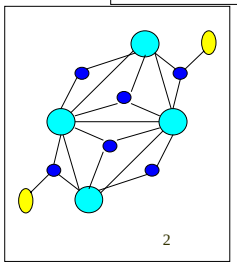
Olesya A. Nikonova, Kjell Jansson, Vadim Kessler, Margareta Sundberg, Alexei I. Baranov, Andrei V. Shevelkov, Pavel A. Shcheglov, Dmitrii V. Drobot and Gulaim A. Seisenbaeva . Electrochemical synthesis, structural characterization and decomposition of rhenium oxoethoxide, Re4O4(OEt)12. Ligand influence on the structure and bonding in the tetranuclear planar rhenium alkoxide clusters. Inorg. Chem.47, 1295-1300.



Models 1, 2.

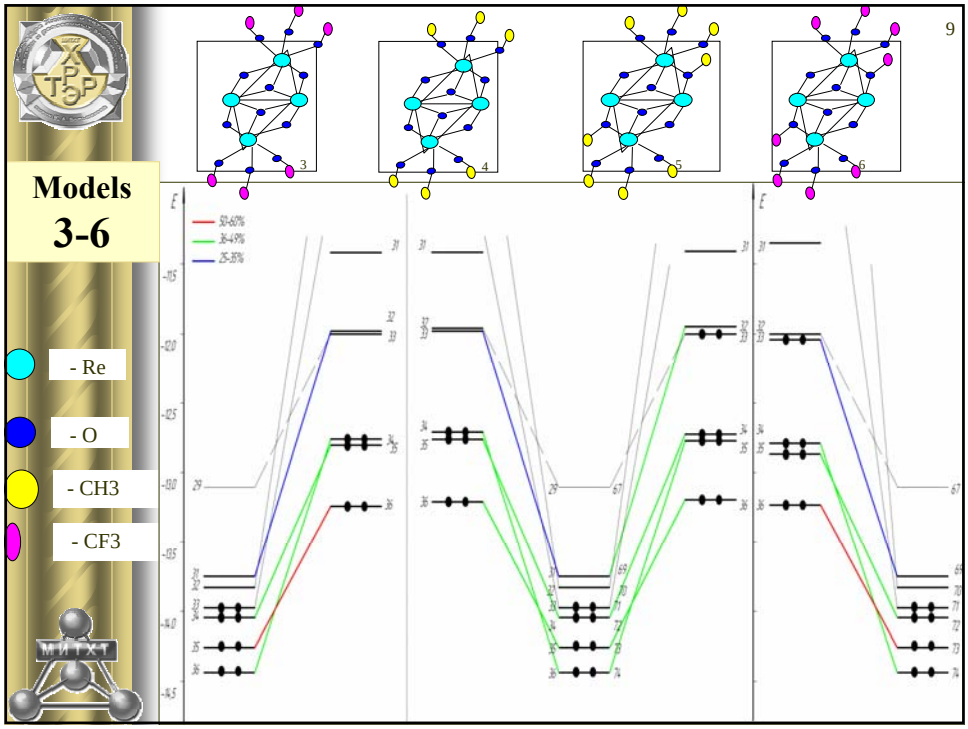


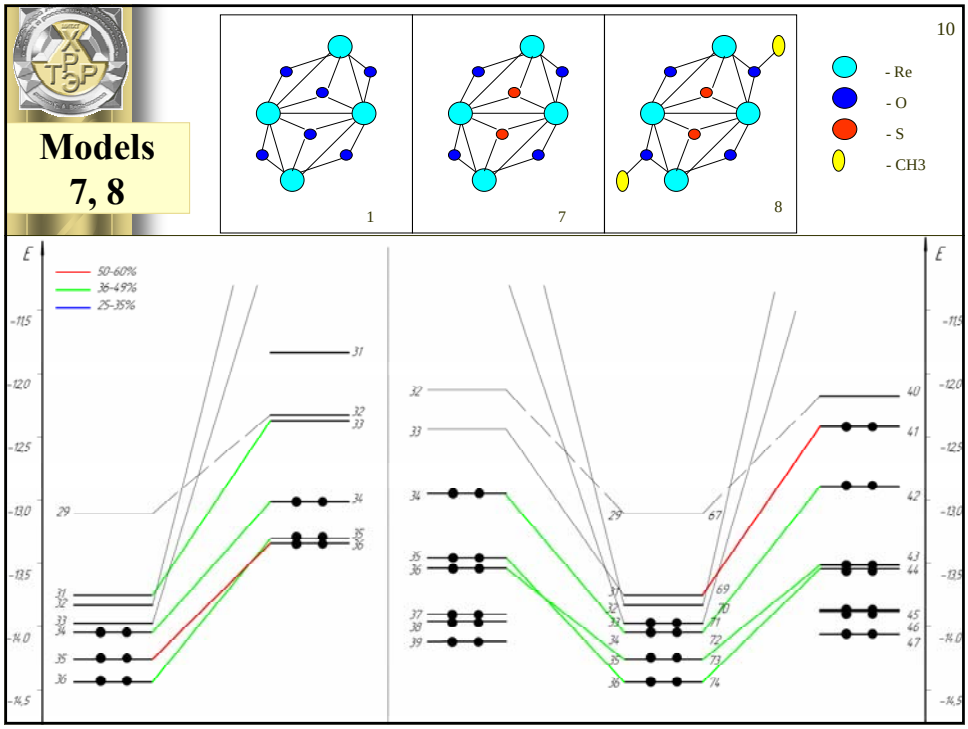
- Re



- O

- CH3


9
Models
3-6
- Re
- O
- CH3
- CF3
3
4
5
6
E
50-60%
35-49%
25-35%


10
Models
7, 8
- Re
- O
- S
- CH3
1
7
8
E
50-60%
35-49%
25-35%

Anodic dissolution of Rhenium in alkohols

Concentration of background electrolyte (LiCl)

C_{LiCl} = 0,1 M; cathode – Pt plate.

№	n(EtOH):n(i-PrOH) in electrolyte	U, *V*	I, *mA*	t, *h.*
I	1:1	110-160	260-80	17
II	2:1	50-100	160-110	26,3
III	1:2	60-150	100-30	24,8

Products of synthesis I -VI were described with X-ray Phase Analysis, Elemental Analysis, DTA and IR-spectroscopy.

№	n(EtOH):n(CF_3CH_2OH) in electrolyte	U, *V*	I, *mA*	t, *h.*
IV	1:1	35-70	170-130	31,7
V	2:1	50-70	195-110	32
VI	0:1	30-60	80-20	37,7

The data of element analysis for the first syntesis in comparison with the literary data.

complex	C, %	H, %	Re, %
[1] $Re_4O_4(OEt)_{12}$	20,25	3,90	55,20
[2] $Re_4O_6(OPr^i)_{10}$	24,20	5,10	52,00
I	9,35	2,10	55,24

[1] **Olesya A. Nikonova, Kjell Jansson, Vadim Kessler, Margareta Sundberg, Alexei I. Baranov, Andrei V. Shevelkov, Pavel A. Shcheglov, Dmitrii V. Drobot and Gulaim A. Seisenbaeva .** Electrochemical synthesis, structural characterization and decomposition of rhenium oxoethoxide, $Re_4O_4(OEt)_{12}$. Ligand influence on the structure and bonding in the tetranuclear planar rhenium alkoxide clusters. Inorg. Chem.47, 1295-1300.

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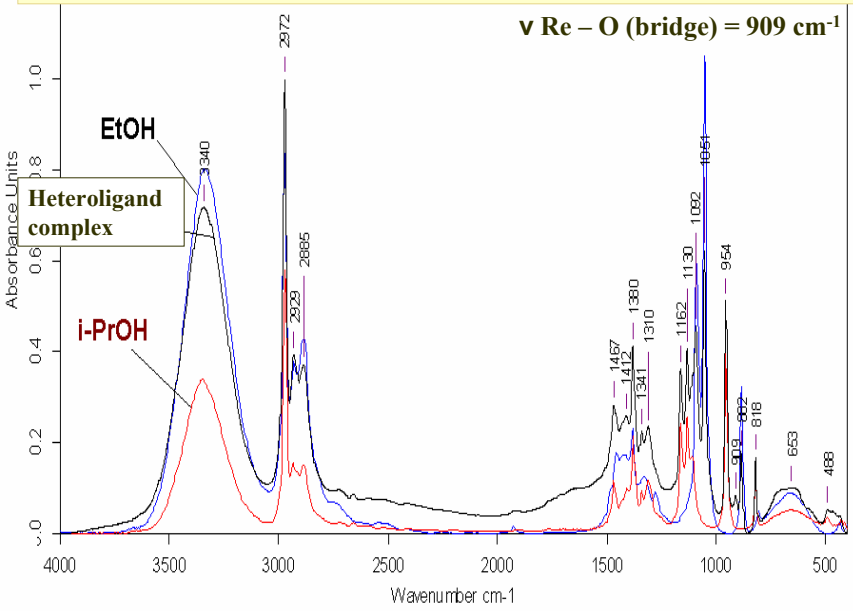
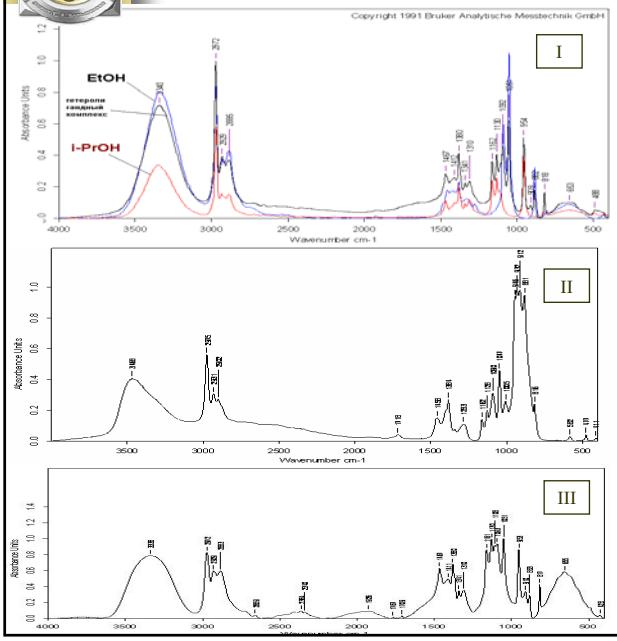
IR-spectrum heteroligand complexes of Rhenium (I).



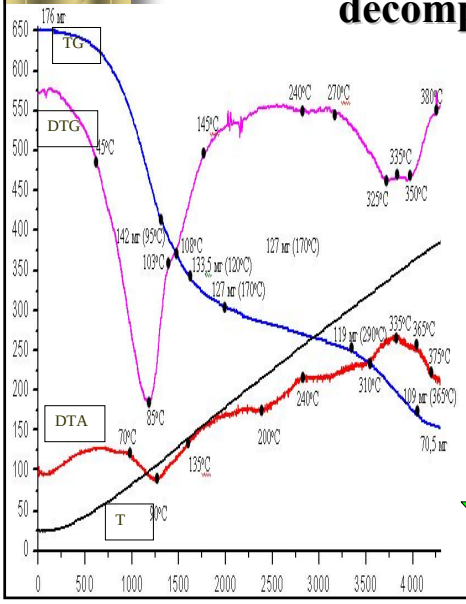
I, II, III IR-spectrum heteroligand complexes of Rhenium.

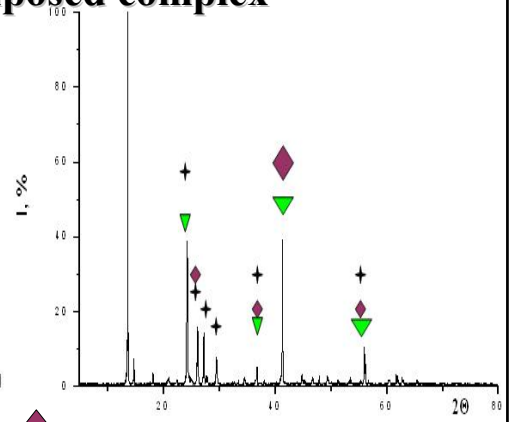


№	Appropriation of frequencies:
I	ν O-H = 3340 ν C-O = 1051-1162 ν C-H = 2885-2972 ν Re=O = 954 ν Re – O (bridge) = 653-902 ν Re – O(R) = 488
II	ν O-H = 3468 ν C-O = 1047-1162 ν C-H = 2902-2975 ν Re=O = 1005 ν Re – O (bridge) = 816 – 946 ν Re – O(R) = 477-582
III	ν O-H = 3470 ν C-O = 1093-1161 ν C-H = 2933-2978 ν Re=O = 961-1001 ν Re – O (bridge) = 913-938 ν Re – O(R) = 477

Table's data produce in cm^{-1}

Thermogramm of heating for the complex IR and X-ray analyses product for the decomposed complex



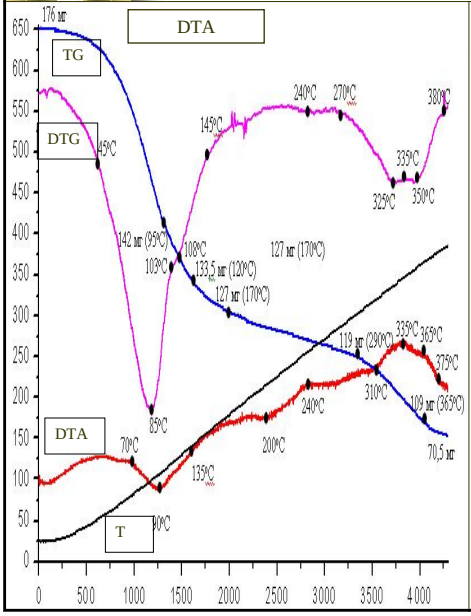


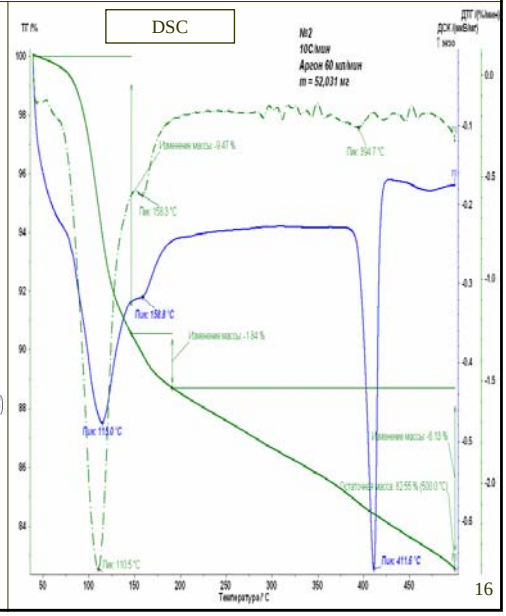
ICDD–JCPDS, No.17-0600, ReO_2 monoclinic

ICDD–JCPDS, No.09-0274, ReO_2 rombouse

PSC TI40/11S, Re_3O_{10} *

DTA (in the open air) and DSC (in Ar) curves for the heteroligands complex I.





conclusions.

- The forming of complexes based on $Re_4O_6(OPr^i)_{10}$ structure and one based on $Re_4O_4(OEt)_{12}$ is equiprobable.

- In the $Re_4O_4(OEt)_{12}$ the part of -(OEt) ligands can be substitute on -(CH_2CF_3) ligands. Substitution atoms of H on F rise up the stability of complex in the case when it occures in the μ_2 position.

- The structure with the Re_4 cluster-frame can exist, and μ_3-**O** ligands in it can be substitute on μ_3-**S** ligands. And the S containing complex will be more stable than the another one.

Gratitudes.

- **Prof. D.V. Drobot**
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- **Prof. A.V. Shevelkov**
Lomonosov Moscow State University, Department of Chemistry, Moscow.

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- **work group - I.V.Mazilin, K.A. Smirnova, O.V.Petrakova**

*Thomas Hartmann. **Preparation, characterization and physical properties of new compounds in the system Ln2O3 – ReO2 – ½ Re2O7 (Ln = lanthanides or yttrium).** // zur Erlangung des akademischen Grades eines Dr.-Ing. genehmigte Dissertation von. Vom Fachbereich Material- und Geowissenschaften der Technischen Universität Darmstadt. Darmstadt. 2004.