



RECENT RESULTS IN RHENIUM CLUSTER CHEMISTRY

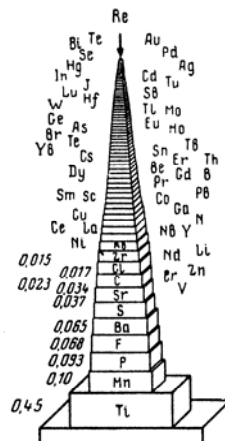
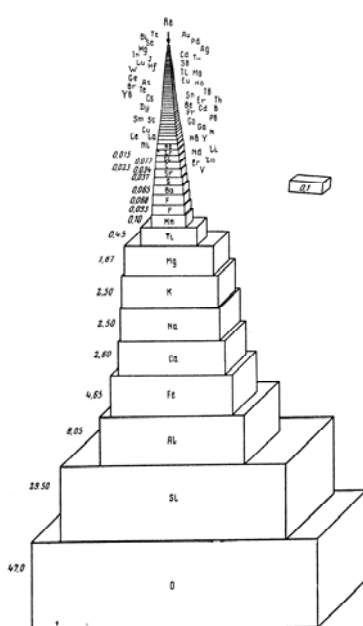
V.E. Fedorov, Yu.V. Mironov,
N.G. Naumov, K.A. Brylev

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Siberian Branch of Russian Academy of Sciences
Novosibirsk, Russia*



*Nikolaev Institute
Inorganic Chemistry
SB RAS*

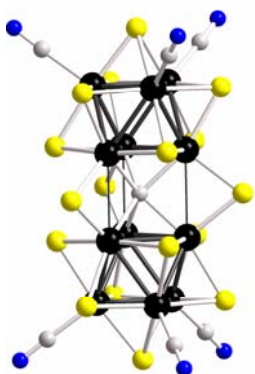
Elements content in the earth's crust (weigh%)



**weigh clark
of rhenium:
~ 5 · 10⁻⁷ %**

Discovery of rhenium:

W.Noddack, I.Tacke,
Naturwiss., 1925, 13, 567.



Laboratory of
SYNTHESIS
of cluster compounds
and materials

Coordination Chemistry
Department

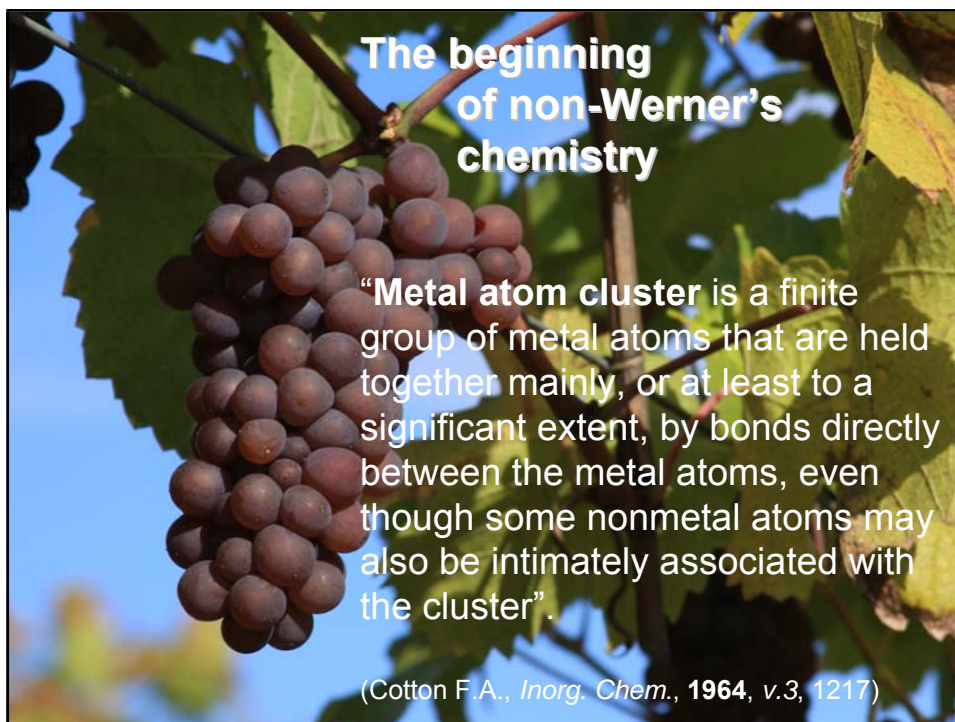


*Nikolaev Institute
of Inorganic Chemistry
SB RAS*

“In the beginning was the **WORD...**”
The Bible. The Word of God.

In the beginning
of chemistry was
SYNTHESIS





Chalcogenides, halides and chalcahalides of the early transition metals (V, Nb, Ta, Mo, W, Re) are typical cluster compounds.

Современная периодическая система элементов Д.И.Менделеева

<p>1 H 1.00794 Hydrogen Водород</p> <p>2 He 4.002602 Helium Гелий</p>	<p>Атомная масса, относительная Атомный номер, Обозначение Распределение электронов Температура плавления (°C) Температура кипения (°C) Электродригательность (по Полювину Аллради и Рохову)</p>																<p>3 Li 6.941 Lithium Литий</p> <p>4 Be 9.012182 Beryllium Бериллий</p>	<p>5 B 10.811 Boron Бор</p> <p>6 C 12.011 Carbon Углерод</p> <p>7 N 14.0074 Nitrogen Азот</p> <p>8 O 15.9994 Oxygen Кислород</p> <p>9 F 18.9984032 Fluorine Фтор</p> <p>10 Ne 20.1797 Neon Неон</p>
<p>11 Na 22.989770 Sodium Натрий</p> <p>12 Mg 24.3050 Magnesium Магний</p>	<p>13 Al 26.981538 Aluminum Алюминий</p> <p>14 Si 28.08558 Silicon Кремний</p> <p>15 P 30.973762 Phosphorus Фосфор</p> <p>16 S 32.06 Sulfur Сера</p> <p>17 Cl 35.453 Chlorine Хлор</p> <p>18 Ar 39.948 Argon Аргон</p>	<p>19 K 39.0983 Potassium Калий</p> <p>20 Ca 40.078 Calcium Кальций</p> <p>21 Sc 44.955910 Scandium Скандий</p> <p>22 Ti 47.88 Titanium Титан</p> <p>23 V 50.9415 Vanadium Ванадий</p> <p>24 Cr 51.9961 Chromium Хром</p> <p>25 Mn 54.938046 Manganese Марганец</p> <p>26 Fe 55.845 Iron Железо</p> <p>27 Co 58.933200 Cobalt Кобальт</p> <p>28 Ni 58.6934 Nickel Никель</p> <p>29 Cu 63.546 Copper Медь</p> <p>30 Zn 65.38 Zinc Цинк</p> <p>31 Ga 69.723 Gallium Галлий</p> <p>32 Ge 72.61 Germanium Германий</p> <p>33 As 74.92160 Arsenic Арсен</p> <p>34 Se 78.96 Selenium Селен</p> <p>35 Br 79.904 Bromine Бром</p> <p>36 Kr 83.80 Krypton Криптон</p>																
<p>37 Rb 85.4678 Rubidium Рубидий</p> <p>38 Sr 87.62 Strontium Стронций</p> <p>39 Y 88.90585 Yttrium Иттрий</p> <p>40 Zr 91.224 Zirconium Цирконий</p> <p>41 Nb 92.90638 Niobium Нобий</p> <p>42 Mo 95.94 Molybdenum Молибден</p> <p>43 Tc 98 Technetium Технеций</p> <p>44 Ru 101.07 Ruthenium Рутений</p> <p>45 Rh 101.07 Rhodium Родий</p> <p>46 Pd 106.3675 Palladium Палладий</p> <p>47 Ag 107.8682 Silver Серебро</p> <p>48 Cd 112.411 Cadmium Кадмий</p> <p>49 In 114.818 Indium Индий</p> <p>50 Sn 118.710 Tin Олово</p> <p>51 Sb 121.757 Antimony Сурьма</p> <p>52 Te 127.60 Tellurium Теллур</p> <p>53 I 126.90545 Iodine Йод</p> <p>54 Xe 131.29 Xenon Ксенон</p>	<p>55 Cs 132.90545 Cesium Цезий</p> <p>56 Ba 137.327 Barium Барий</p> <p>57 La 138.90547 Lanthanum Лантан</p> <p>58 Ce 140.90765 Cerium Церий</p> <p>59 Pr 140.90765 Praseodymium Прометий</p> <p>60 Nd 144.24 Neodymium Неодим</p> <p>61 Pm 144.91288 Promethium Прометий</p> <p>62 Sm 150.36 Samarium Самарий</p> <p>63 Eu 151.964 Europium Европий</p> <p>64 Gd 157.25 Gadolinium Гадолий</p> <p>65 Tb 158.92534 Terbium Тербий</p> <p>66 Dy 162.50 Dysprosium Диспрозий</p> <p>67 Ho 164.93032 Holmium Гольмий</p> <p>68 Er 167.26 Erbium Эрбий</p> <p>69 Tm 168.930421 Thulium Тим</p> <p>70 Yb 173.04 Ytterbium Иттербий</p> <p>71 Lu 174.967 Lutetium Лютеций</p>																	

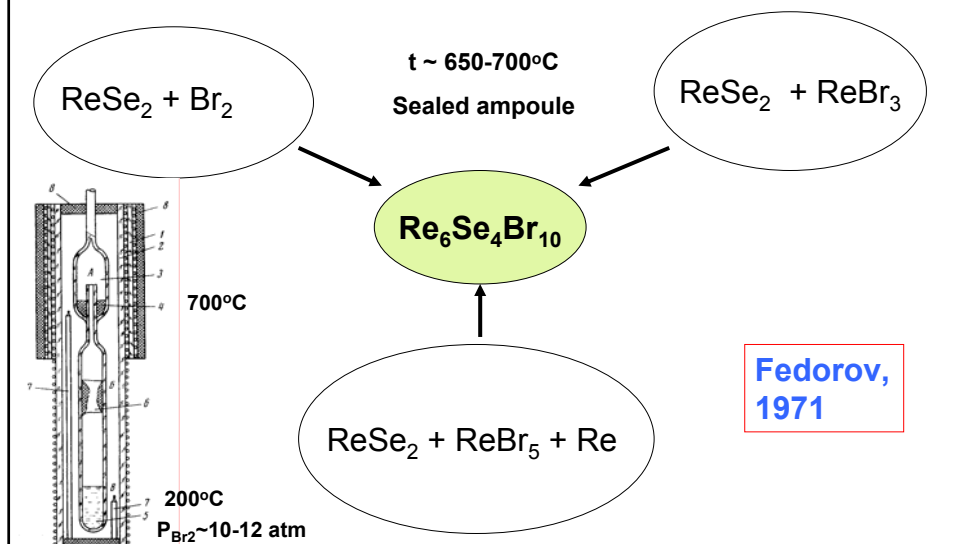
Ionic radii of chalcogenide and halide ligands, Å

S²⁻	1.82	Cl⁻	1.81
Se²⁻	1.93	Br⁻	1.96
Te²⁻	2.11	I⁻	2.20

Crystallo-chemical similarity of chalcogenide and halide ions
but
Difference of their electronic properties

Chalcogenide and halide anions are stabilizing π-ligands for “high-valency” cluster complexes of the transition metals.

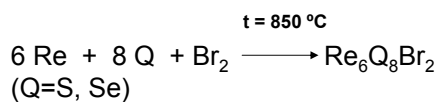
Syntheses of octahedral rhenium cluster complex $\text{Re}_6\text{Se}_4\text{Br}_{10}$



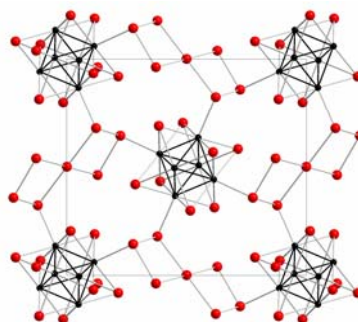
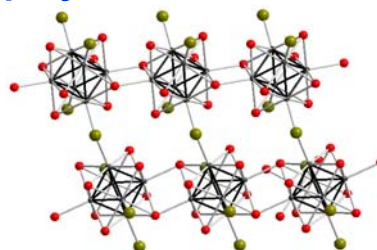
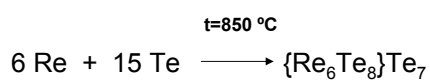
About thermodynamic stability of cluster compounds...

- $\text{ReSe}_2 + 5 \text{Br}_2 (\text{excess}) \rightarrow \text{Re}_6\text{Se}_4\text{Br}_{10}$
 $\text{Re}^{4+} \rightarrow \text{Re}^{3+}$
- $2\text{ReSe}_2 + 4 \text{ReBr}_3 \rightarrow \text{Re}_6\text{Se}_4\text{Br}_{10} + \text{Br}_2$
 $\text{Re}^{4+} \quad \text{Re}^{3+} \quad \rightarrow \text{Re}^{3+}$

High temperature solid state synthesis of cluster rhenium compounds having polymeric structures



Ampoule synthesis



The main problem in the chemistry of chalcogenide and chalcohalide cluster compounds is:

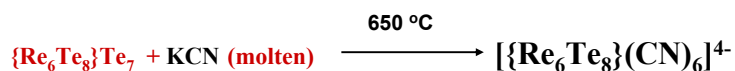
Metal cluster compounds with polymeric structures are not soluble in water and organic solvents

therefore

similar compounds have a very low chemical reactivity.

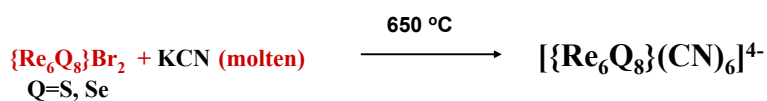
Discovery of octahedral rhenium cluster chalcocyanide complexes $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ (Q=S, Se, Te)

Excision of $\{\text{Re}_6\text{Q}_8\}$ cluster core from polymeric compounds:



A. Slougui, Yu.V. Mironov, A. Perrin, V.E. Fedorov,
Croatica Chemica Acta, 1995, v. 68, pp. 885-890.

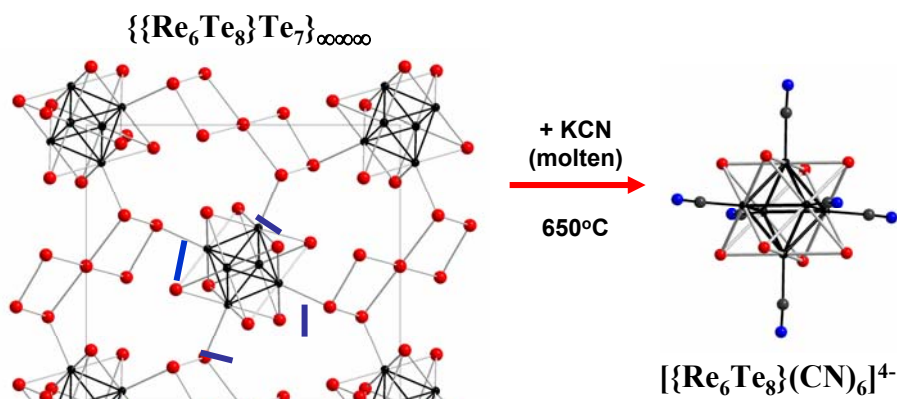
Yu.V. Mironov, A.V. Virovets, V.E. Fedorov, N.V. Podberezkaya, O.V. Shishkin, Yu.T. Struchkov,
Polyhedron, 1995, v.14, pp.3171-3173.



N.G. Naumov, A.V. Virovets, N.V. Podberezkaya, V.E. Fedorov,
Russ. J. Struct. Chem., 1997, v.38, pp.857-862.

H. Imoto, N.G. Naumov, A.V. Virovets, T. Saito, V.E. Fedorov,
Russ. J. Struct. Chem., 1998, v.39, pp.720-727.

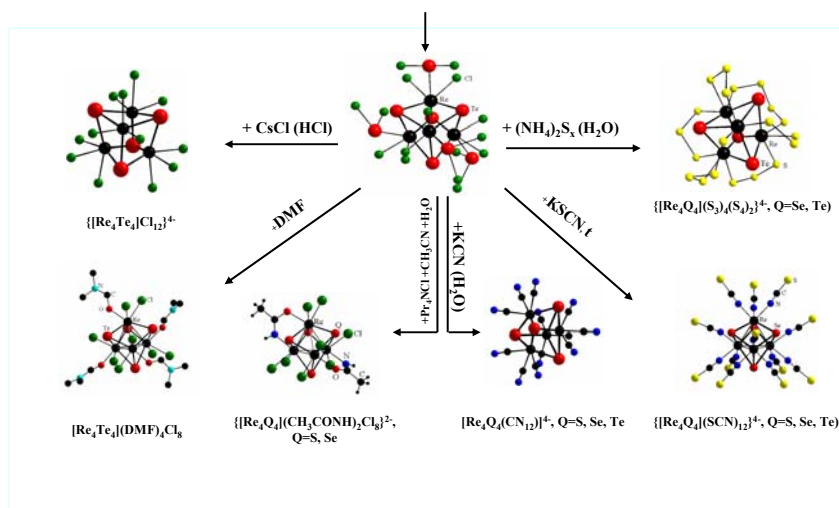
Schematic presentation of excision of cluster core $\{\text{Re}_6\text{Te}_8\}$ from polymeric rhenium telluride $[\{\text{Re}_6\text{Te}_8\}\text{Te}_7]$ and its transformation in anionic complex $[\{\text{Re}_6\text{Te}_8\}(\text{CN})_6]^{4-}$



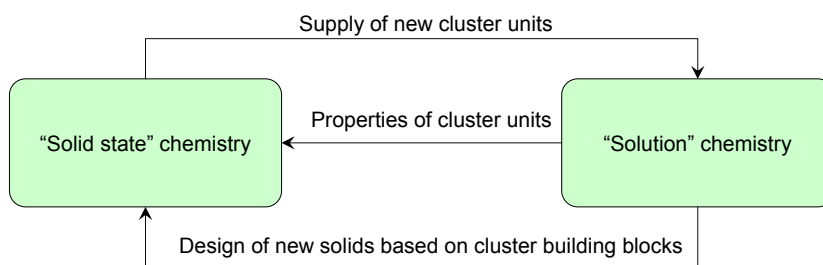
Polymeric $\text{Re}_6\text{Te}_{15}$ is **not soluble**

The salts containing this anion
are **high soluble** in water and
some organic solvents.

Transformations of tetrahedral cluster rhenium complexes



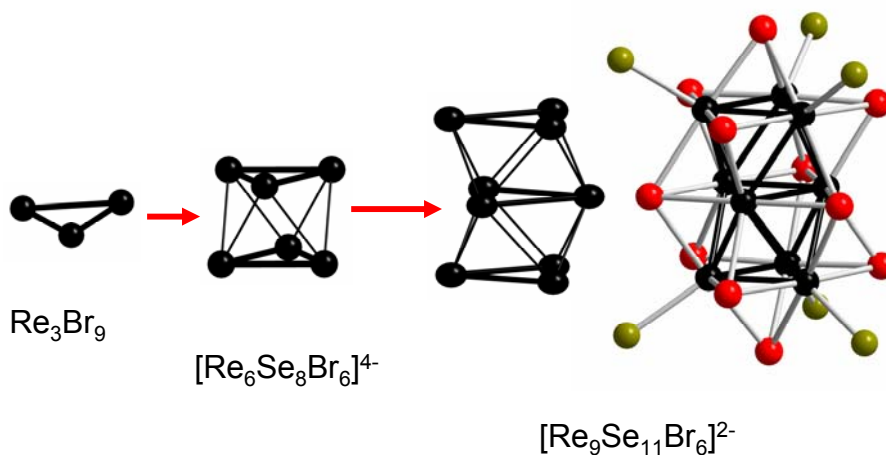
Interconnections between “solid state” and “solution” cluster chemistries



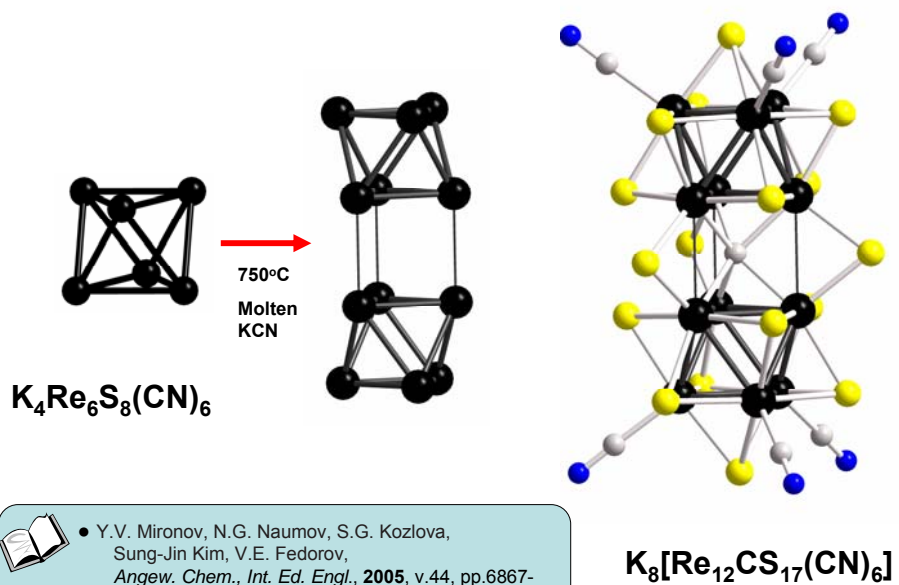
Properties of clusters that should be studied in molecular form:

- Local symmetry / disorder in cluster core;
- Redox properties;
- Electronic spectroscopy / vibrational spectroscopy / NMR
- Others...

Progressive condensation of cluster fragments
in the high temperature reaction $\text{Re}_3\text{Br}_9 + \text{CdSe}$

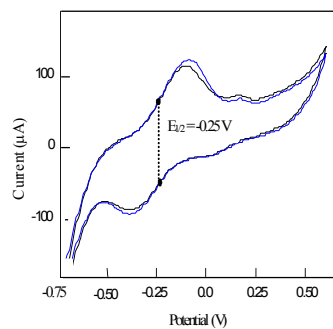
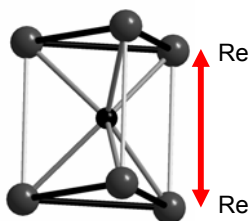
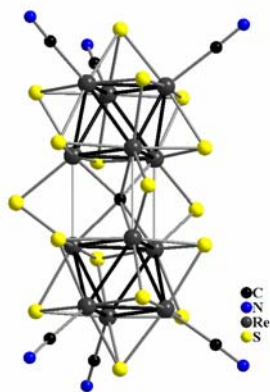


“Condensation” of octahedral cluster fragments



• Y.V. Mironov, N.G. Naumov, S.G. Kozlova,
Sung-Jin Kim, V.E. Fedorov,
Angew. Chem., Int. Ed. Engl., **2005**, v.44, pp.6867-
6871.

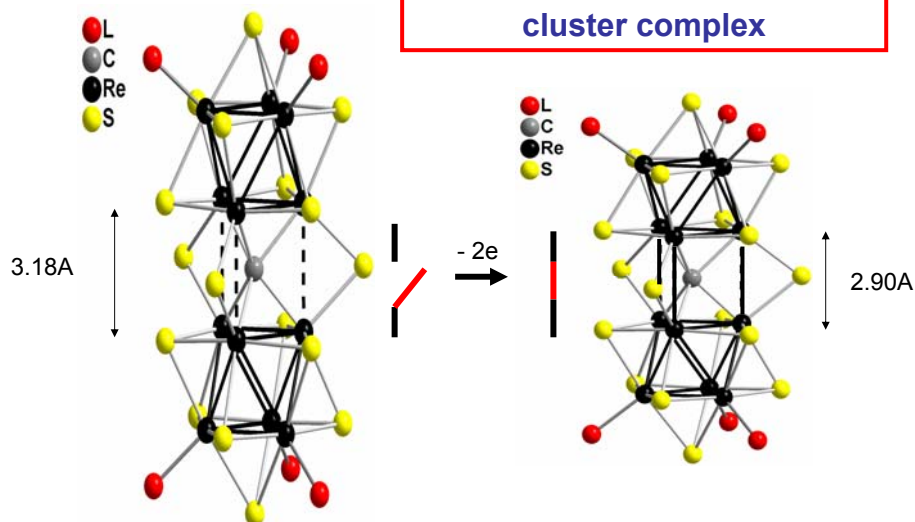
The structure of cluster anions $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{6-/8-}$



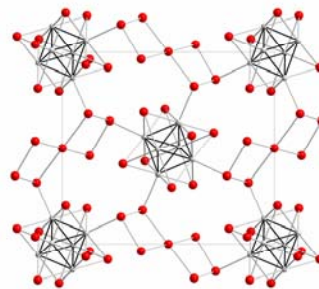
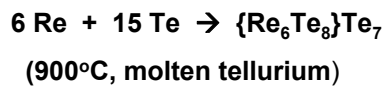
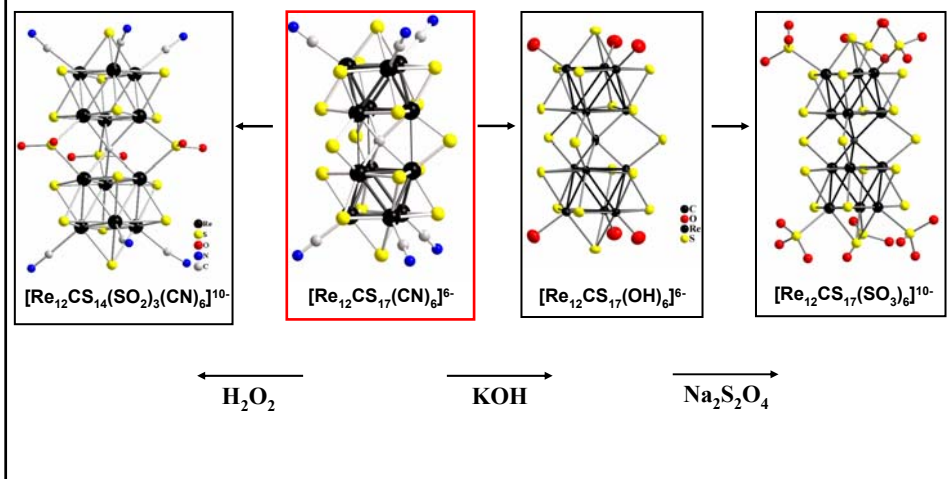
Anion 8- Re-Re = 3.178-3.184 Å

Anion 6- Re-Re = 2.904 Å

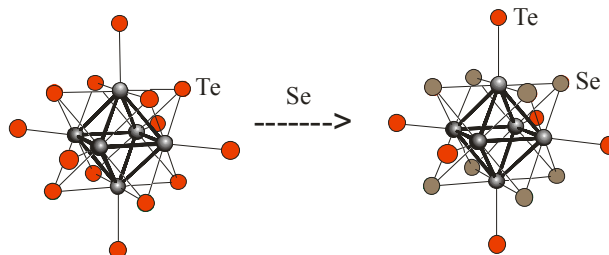
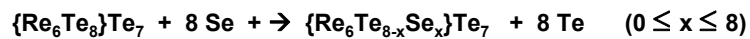
One molecule electronic switch based on rhenium cluster complex



Chemical modification of ligand environment
in cluster complex $K_6[Re_{12}CS_{17}(CN)_6]$

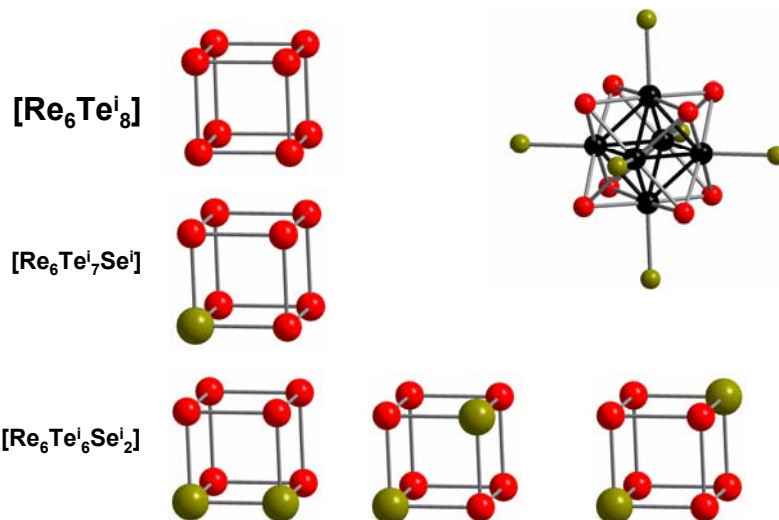


Substitution of inner μ_3 -Te ligands in cluster core $\{Re_6Te_8\}$ by Se atoms:



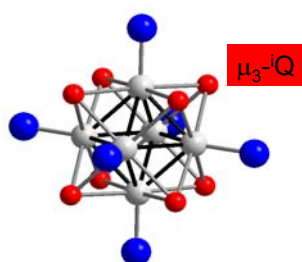
Octahedral mixed-ligands clusters

Distribution of inner ligands in cluster core $[\text{Re}_6\text{Te}_{8-x}\text{Se}_x]$



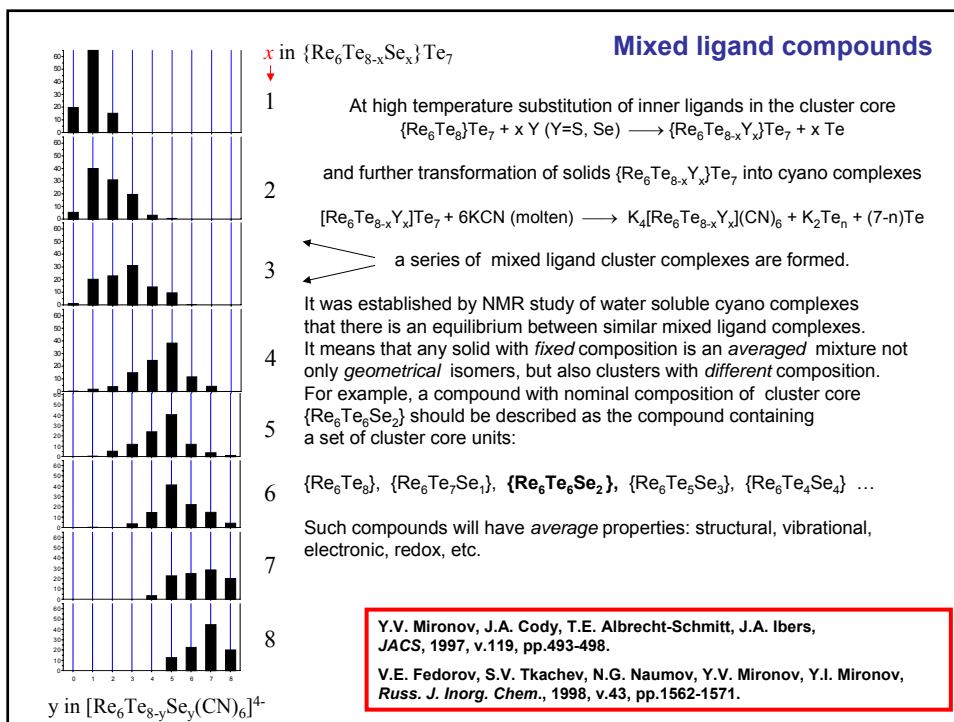
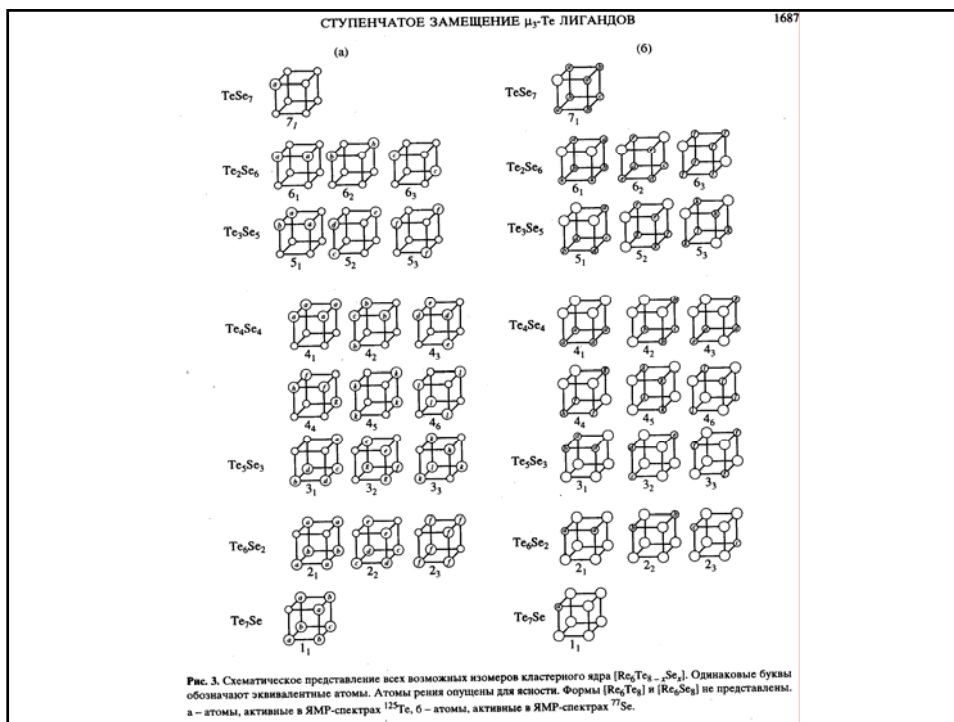
Expected ratio of isomers 3 : 3 : 1

Possible numbers of isomers in mixed ligand cluster cores $[\text{Re}_6(\mu_3\text{-Q})_8]$ (Q = Te, Se)



Re_6Te_8	1
$\text{Re}_6\text{Te}_7\text{Se}_1$	1
$\text{Re}_6\text{Te}_6\text{Se}_2$	3
$\text{Re}_6\text{Te}_5\text{Se}_3$	3
$\text{Re}_6\text{Te}_4\text{Se}_4$	6
$\text{Re}_6\text{Te}_3\text{Se}_5$	3
$\text{Re}_6\text{Te}_2\text{Se}_6$	3
$\text{Re}_6\text{Te}_1\text{Se}_7$	1
Re_6Se_8	1

In sum : **22**



Octahedral rhenium(III) cluster complexes

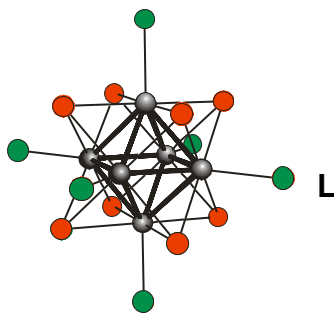


Q=S, Se, Te, Cl, Br, O

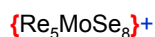
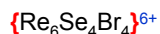
L=Cl, Br, I, OH, CN, SCN...

N-, P-, O-, S- donor organic ligands

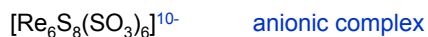
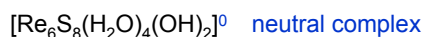
Re - Re 2.60-2.66Å



Cluster cores:

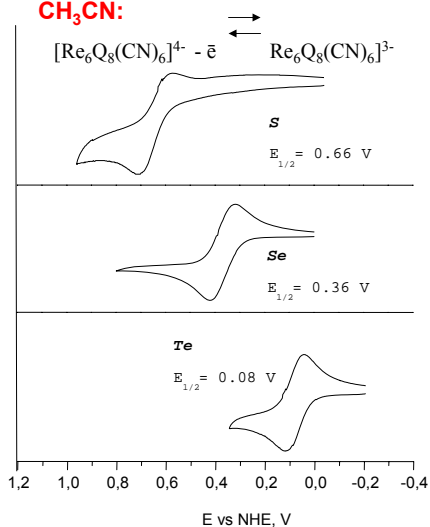


Cluster complexes:

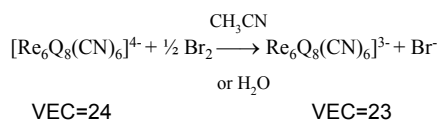


Properties of cluster anions [Re₆Q₈(CN)₆]ⁿ⁻ (Q= S, Se, Te)

Electro-chemical behavior in
CH₃CN:



Chemical oxidation:



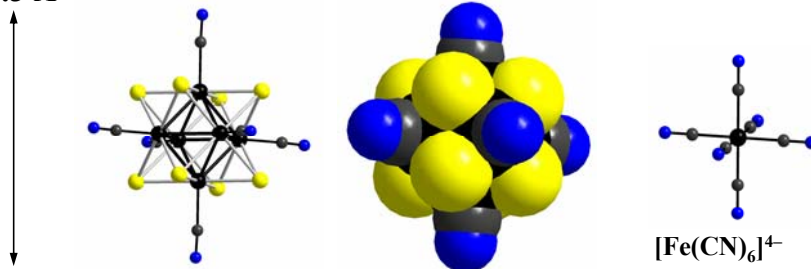
Magnetic moments of the compounds
containing oxidized anions
[Re₆Q₈(CN)₆]³⁻ (VEC=23)

Compounds	μ_{eff} , BM (T=298K)
(PPh ₄) ₃ [Re ₆ S ₈ (CN) ₆]	1.9
(PPh ₄) ₂ (H)[Re ₆ Se ₈ (CN) ₆].4H ₂ O	1.8
(NBu ₄) ₂ (H)[Re ₆ Te ₈ (CN) ₆]	1.9

In rhenium chalcocyanide complexes $[\text{Re}_6(\mu_3\text{-Q})_8(\text{CN})_6]^{n-}$ six metal atoms form an octahedron cluster Re_6 . Eight μ_3 chalcogene ligands (S, Se, or Te) form a cube around the octahedron Re_6 . Six terminal CN-ligands are coordinated to each rhenium atom via carbon. CN ligands are ambidentate and able to coordinate to other metals via N atoms. The anions $[\text{Re}_6(\mu_3\text{-Q})_8(\text{CN})_6]^{n-}$ can be considered as geometrical analogs of mononuclear cyanide complex $[\text{Fe}(\text{CN})_6]^{4-}$ but possessing larger linear and voluminous sizes due to cluster core $\{\text{Re}_6\text{Q}_8\}^{2+}$.

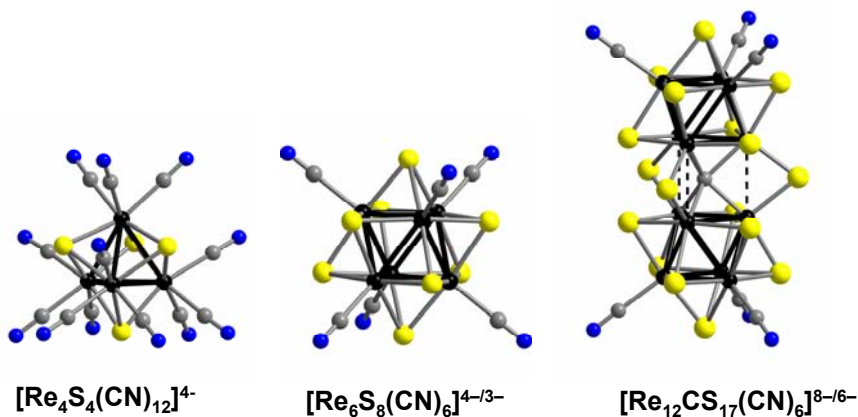
These cluster anions can be used as building blocks in design of coordination polymers.

10.3 Å



Cyanide cluster rhenium complexes

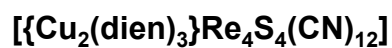
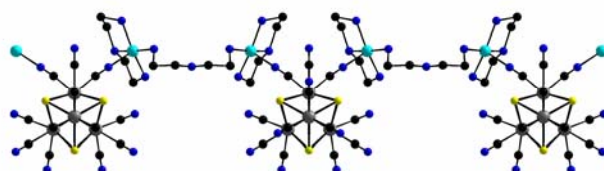
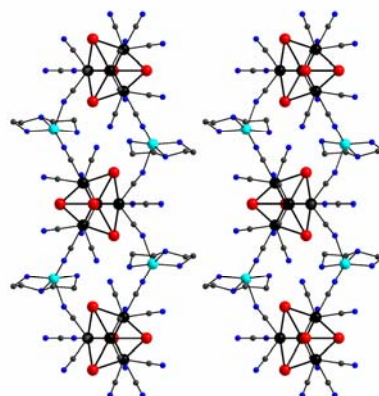
$[\text{Re}_4\text{S}_4(\text{CN})_{12}]^{4-}$, $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-/3-}$ and $[\text{Re}_{12}\text{CS}_{17}(\text{CN})_6]^{8-/6-}$ as building blocks in the design of coordination polymers

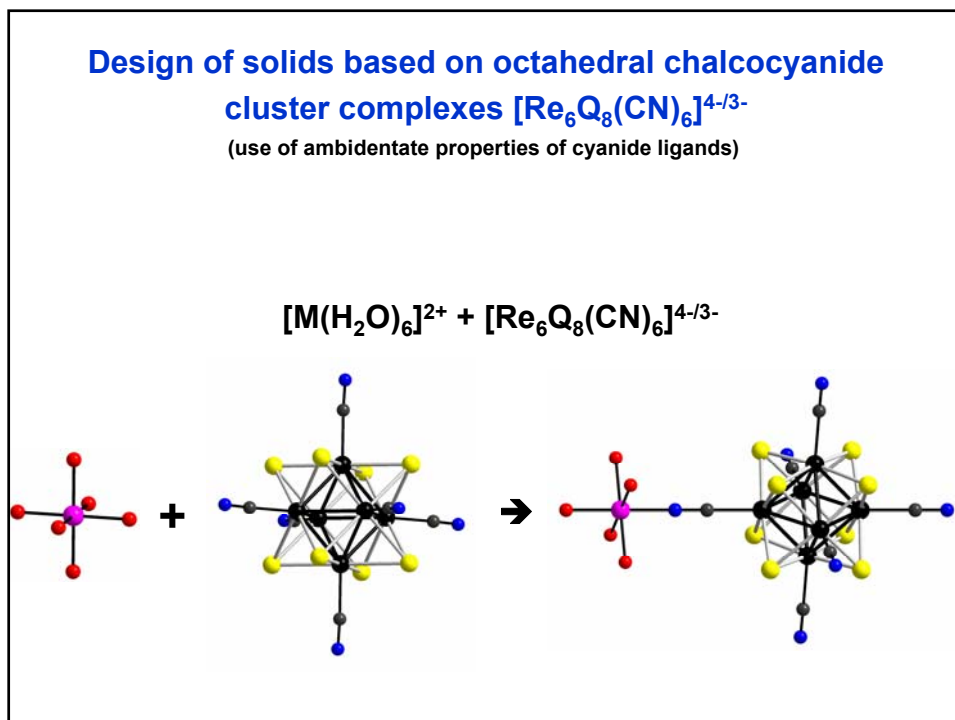
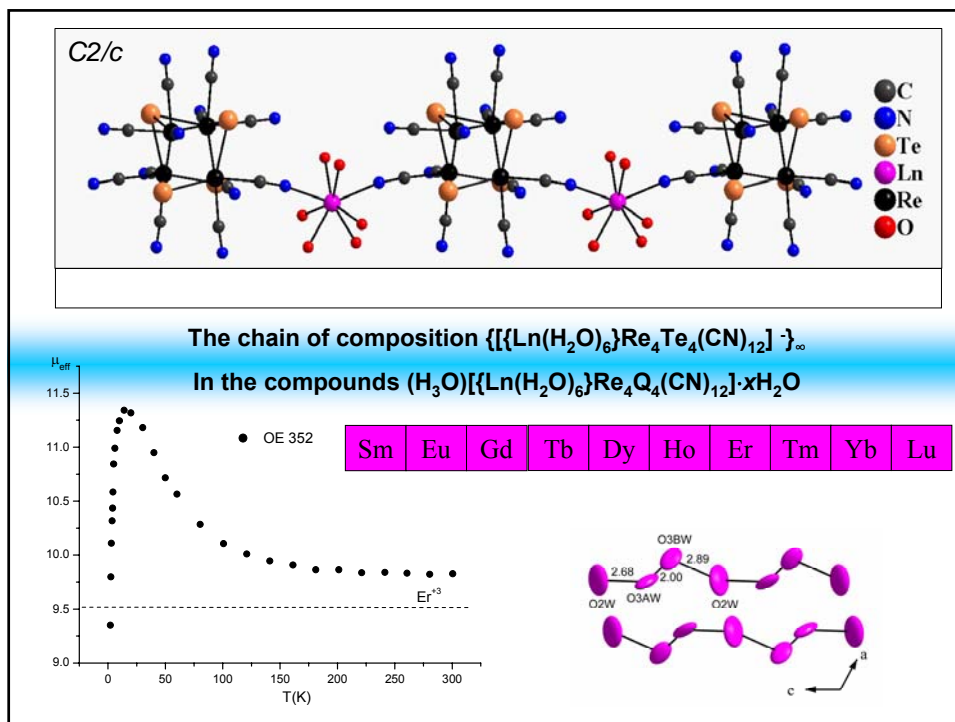


Synthetic approach:

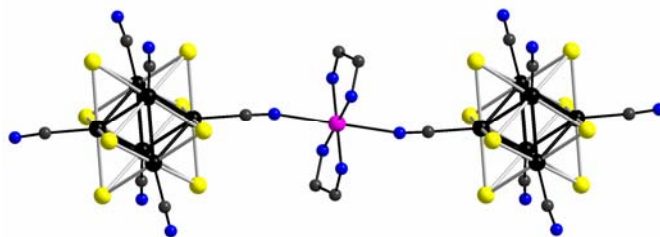
From polymeric compounds
towards molecular complexes
and back again

Chain-like structures based
on chalcocyanide anions
 $[\text{Re}_4\text{Q}_4(\text{CN})_{12}]^{4-}$

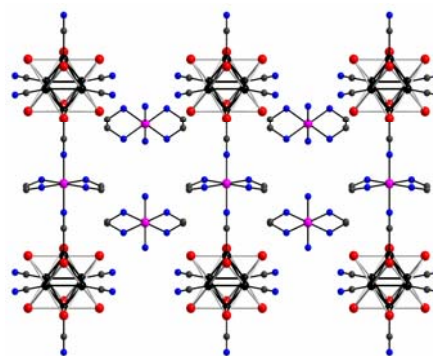
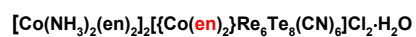
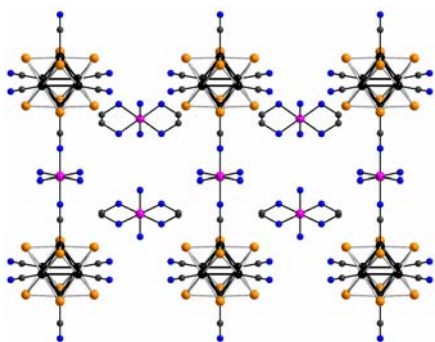
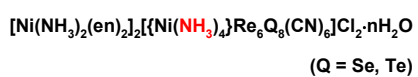




Anionic fragment $[\text{Cu}(\text{en})_2\{\text{Re}_6\text{Te}_8(\text{CN})_6\}_2]^{6-}$
 in the structure $(\text{Et}_4\text{N})_2[\text{CuNH}_3(\text{en})_2]_2[\text{Cu}(\text{en})_2\{\text{Re}_6\text{Te}_8(\text{CN})_6\}_2]\cdot 2\text{H}_2\text{O}$



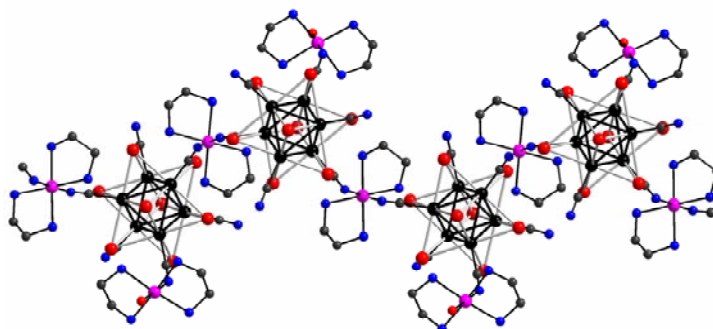
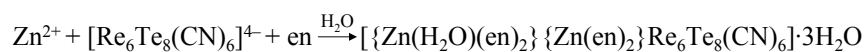
Cluster compounds with infinite cyano-bridged linear chains



H, Se, Te, Cl atoms and water molecules are omitted for clarity

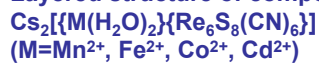
trans-connections

Structures with infinite zig-zag cyano-bridged chains

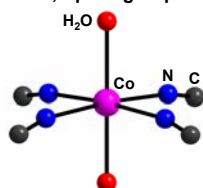


cis-connections

Layered structure of compounds



Orthorhombic, Space group *Imma*



Coordination environment
of Co²⁺ cation

Co-N(NC) 2.16 Å
Co-O(OH₂) 2.05; 2.09 Å
O-Co-O 180°

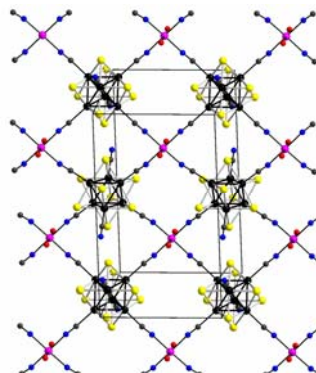
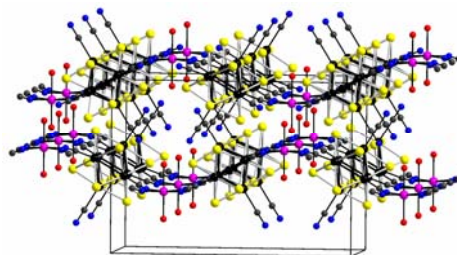
Short S-S contacts:

3.32 Å within layer;
3.67 Å between adjacent layers

Similar structure is not realized for Se

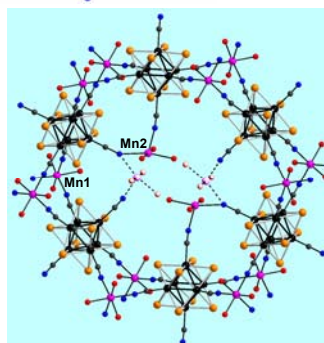
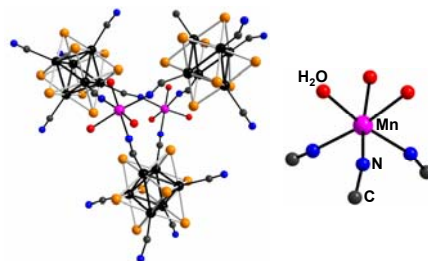
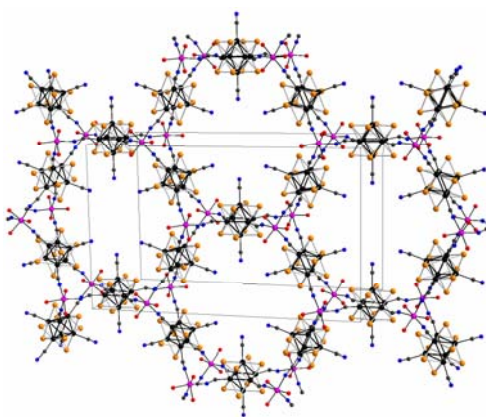
N.G. Naumov, A.V. Virovets, Y.I. Mironov,
S.B. Artemkina, V.E. Fedorov,

Ukraine Chem. J., 1999, v.65, pp.21-27.

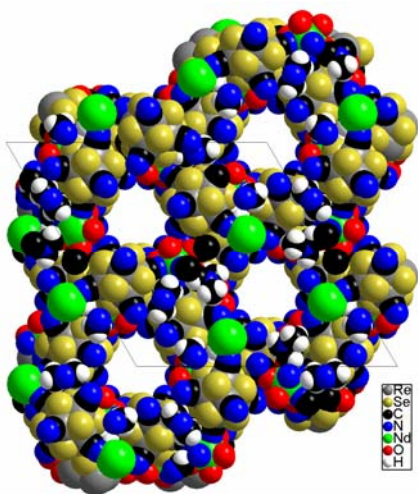


Polymeric structure of compound
 $[\{\text{Mn}(\text{H}_2\text{O})_3\}_2\{\text{Re}_6\text{Se}_8(\text{CN})_6\}]\cdot 3.3\text{H}_2\text{O}$

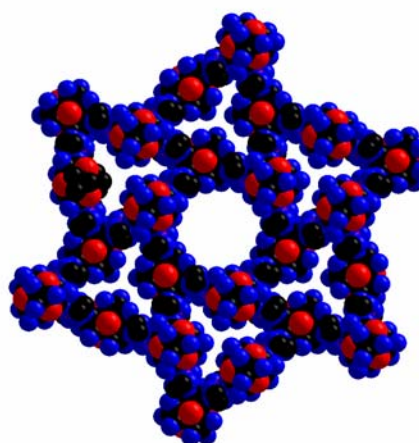
One layer of composition
 $\{\{\text{Mn}(\text{H}_2\text{O})_3\}_4\{\text{Re}_6\text{Se}_8(\text{CN})_6\}_3\}^{4-}_{\infty\infty}$



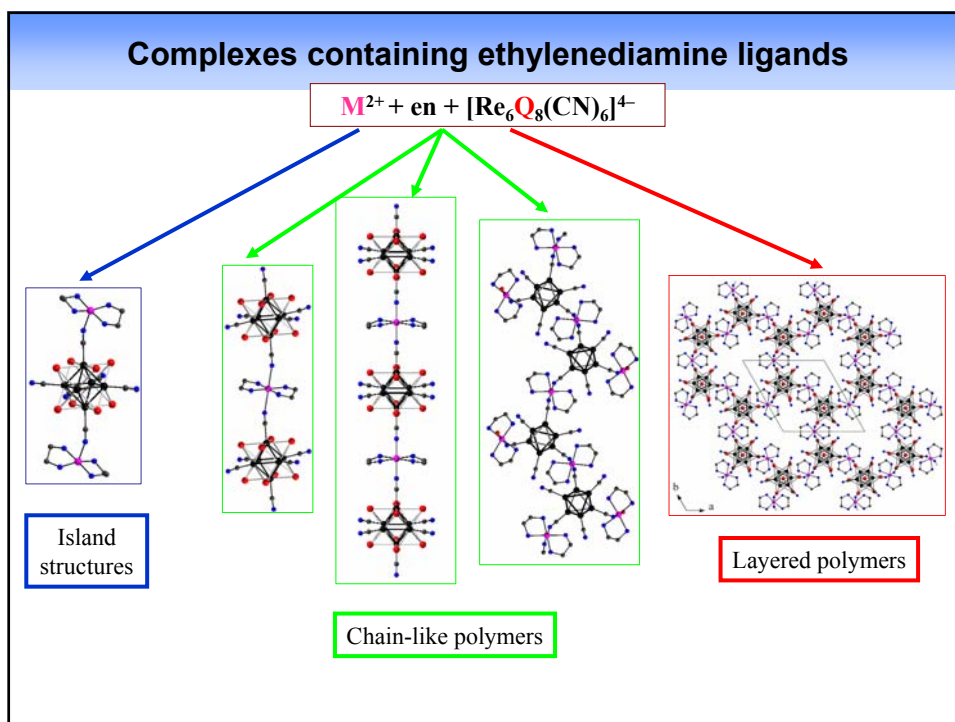
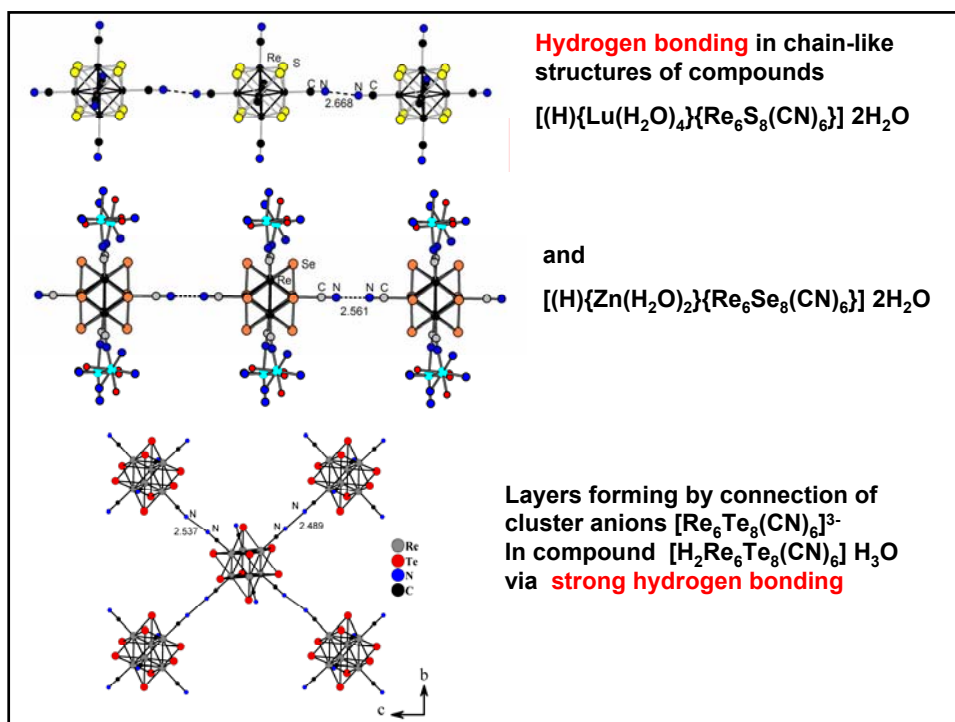
Structures having large one-dimensional channels (~ 8-12 Å)



$(\text{H}_3\text{O})[\{\text{Ln}(\text{H}_2\text{O})_3(\text{dmf})_3\}\{\text{Re}_6\text{Q}_8(\text{CN})_6\}]$
 (Ln = Pr, Nd, Sm, Ho; Q=S, Se, Te)

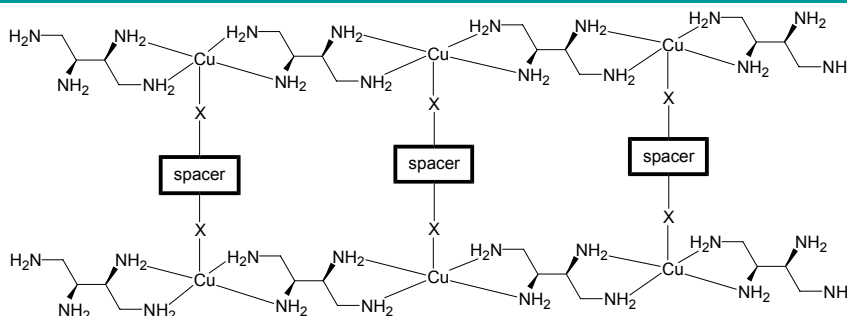
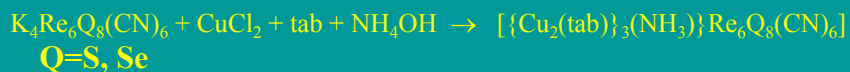
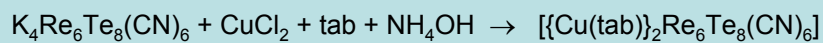


$(\text{NH}_4)_2[\{\text{Ni}(\text{en})_2\}_3\{\text{Re}_4\text{Te}_4(\text{CN})_{12}\}_2]$



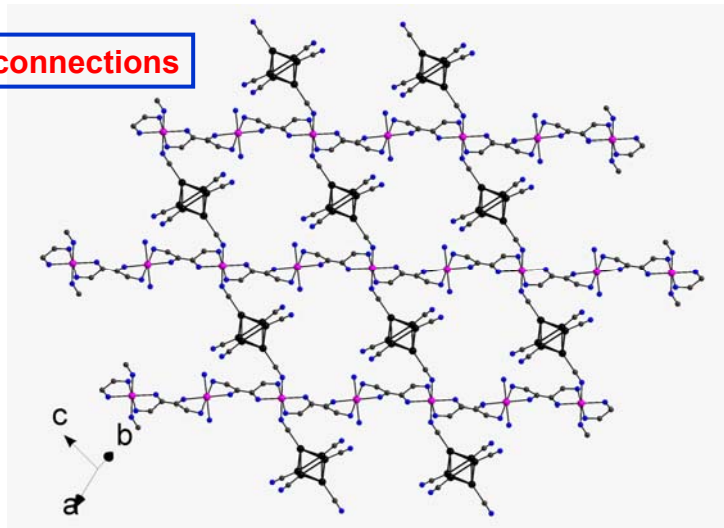
Reactions of cluster anions $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ with cations Cu^{2+} and chiral tetraaminebutane (1,2S,3S,4,- threo-tab)

Y. Mironov, N. Naumov, K. Brylev, O. Efremova, V. Fedorov, K. Hegetschweiler, *Angew. Chem., Int. Ed.*, 2004, v.43, N10, pp.1297-1300.



Flat layer in structure of compound $\{[\text{Cu}_2(\text{tab})_3(\text{NH}_3)]\text{Re}_6\text{Se}_8(\text{CN})_6\} \cdot 2.5\text{H}_2\text{O}$

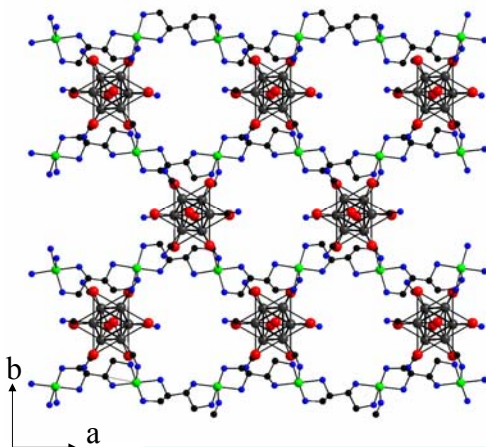
trans-connections



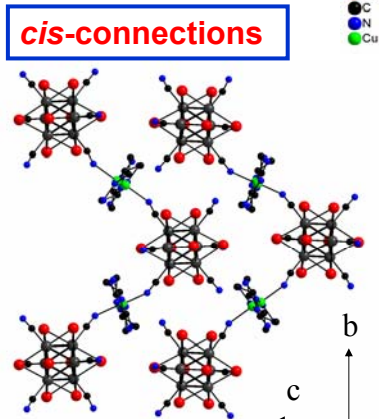
Миронов Ю.В., Наумов Н.Г., Брылев К.А., Ефремова О.А., Федоров В.Е., Хегечвайлер К., *Координационная химия*, 2005, т. 31, №4, с.289-301.

Structure of $\{Cu(tab)\}_2Re_6Te_8(CN)_6\} \cdot 13.5 H_2O$
 Orthorhombic, Space group $P2_12_12_1$, $a = 13.767$, $b = 19.692$, $c = 21.780 \text{ \AA}$

a). One layer

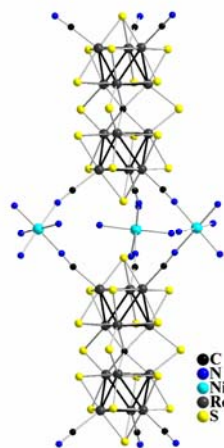
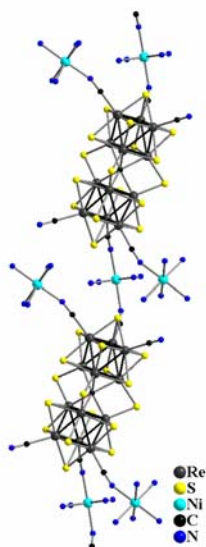
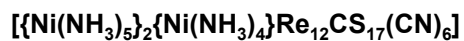


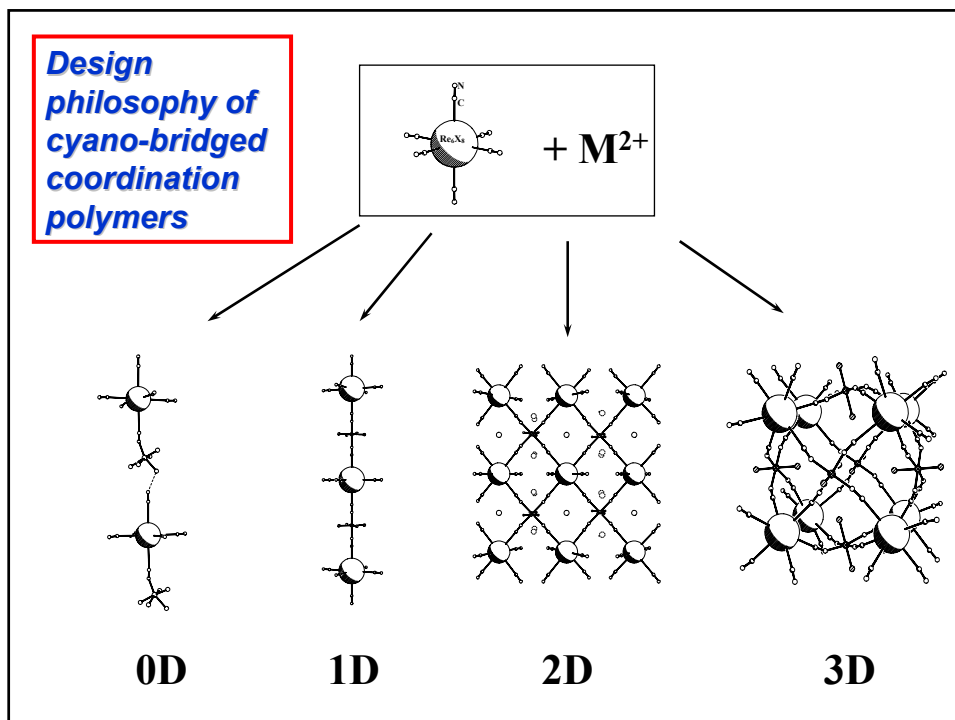
b). Packing wavy layers



Y. Mironov, N. Naumov, K. Brylev, O. Efremova, V. Fedorov, K. Hegetschweiler,
Angew. Chem., Int. Ed., 2004, v.43, N10, pp.1297-1300.

Cyano-bridged complexes based on anion $[Re_{12}CS_{17}(CN)_6]^{6-}$





Cancer therapy

Radiotherapy

$${}^{186}_{75}\text{Re} \xrightarrow{\tau_{1/2} = 90\text{d.}} {}^{186}_{76}\text{Os} + \bar{e}$$

$${}^{188}_{75}\text{Re} \xrightarrow{\tau_{1/2} = 17\text{d.}} {}^{188}_{76}\text{Os} + \bar{e}$$

lung
 ${}^{188}\text{Re}$

Photodynamic therapy (PDT)

$$A + h\nu \longrightarrow A^*$$

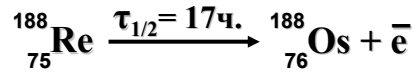
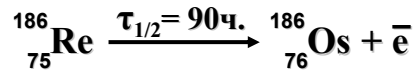
$$A^* \longrightarrow h\nu_1 + A$$

$$h\nu_1 + \text{O}_2(\text{T}) \longrightarrow \text{O}_2(\text{S})$$

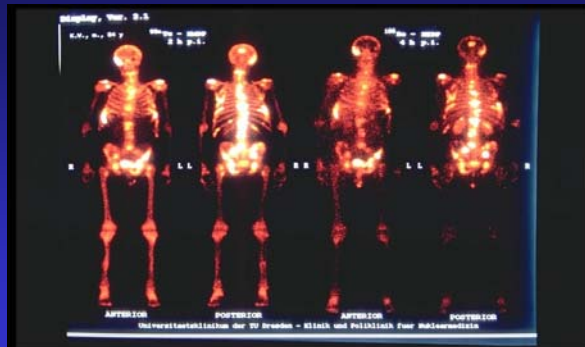
Field of application PDT

Cancer therapy

Radiotherapy

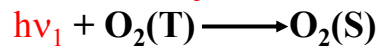
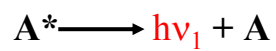
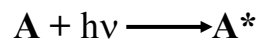


Technetium-Diagnostika und Rhenium-Therapeutika

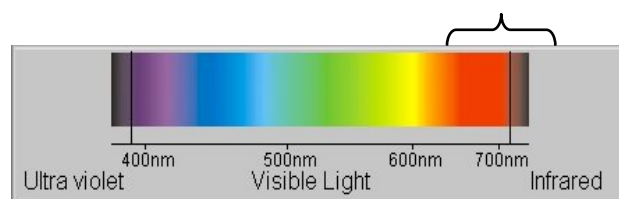


Cancer therapy

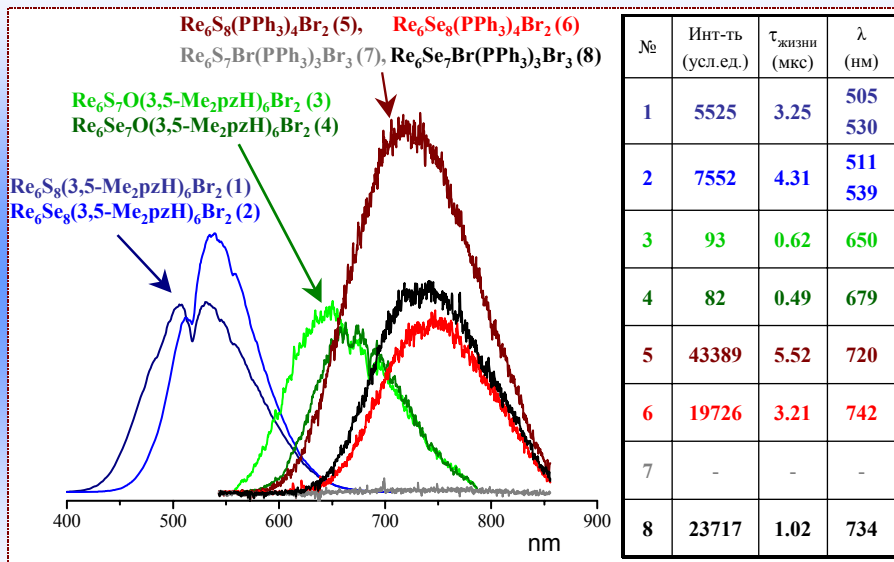
Photodynamic therapy (PDT)



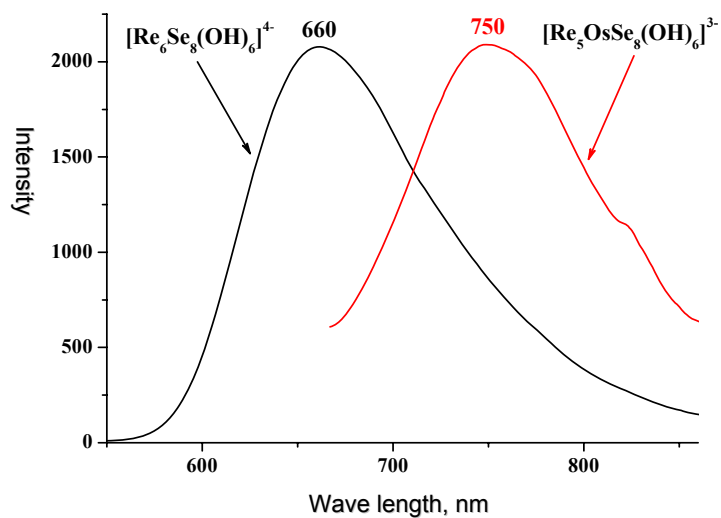
Field of
application
PDT

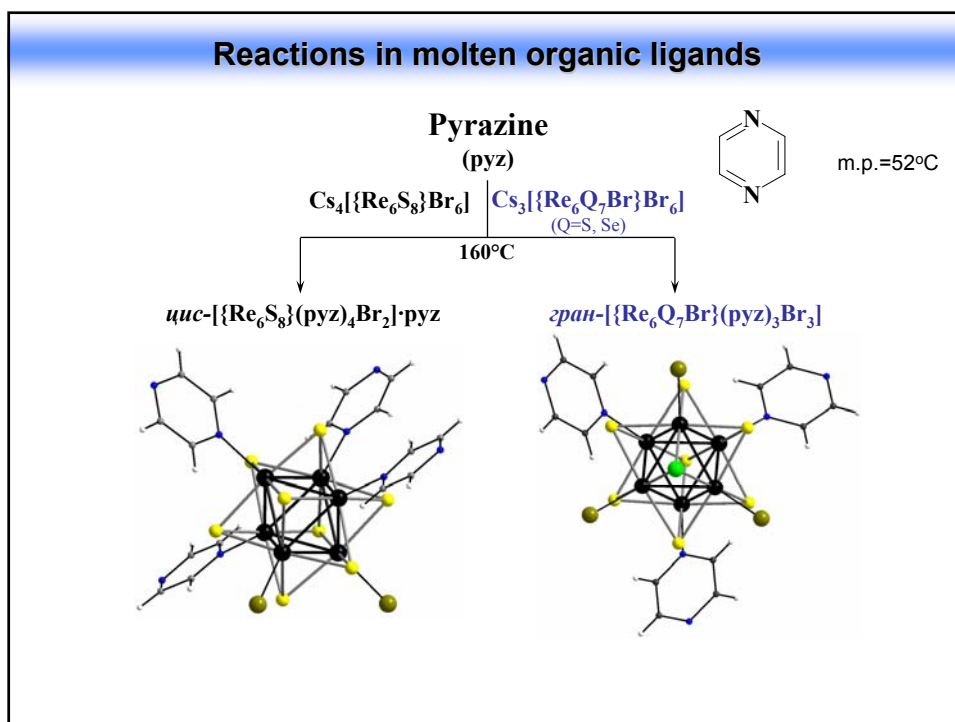
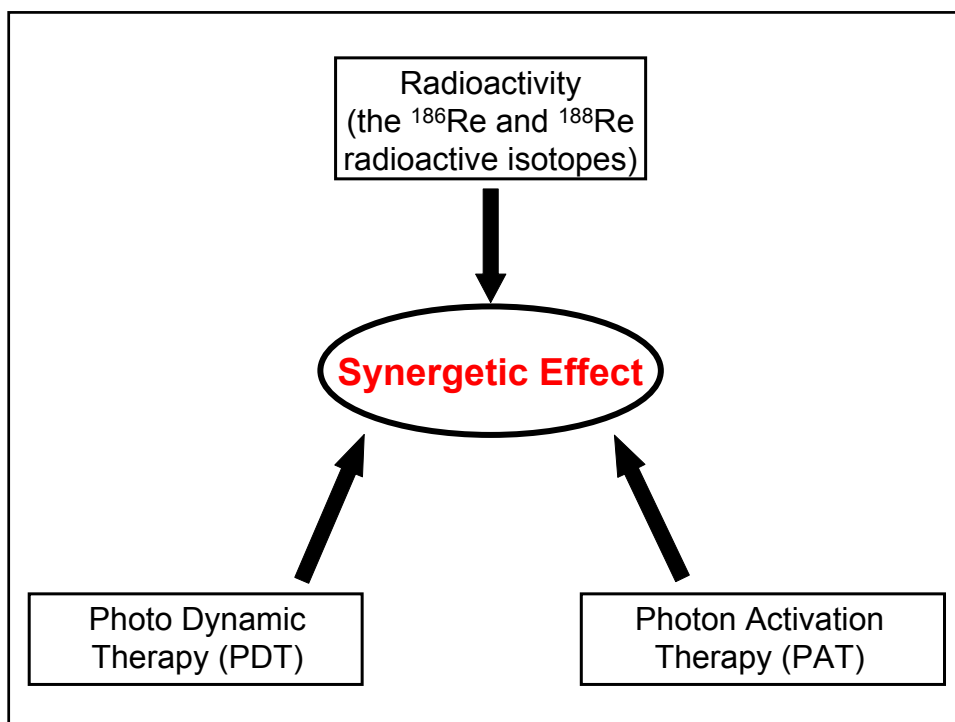


Luminescent properties of octahedral cluster rhenium complexes

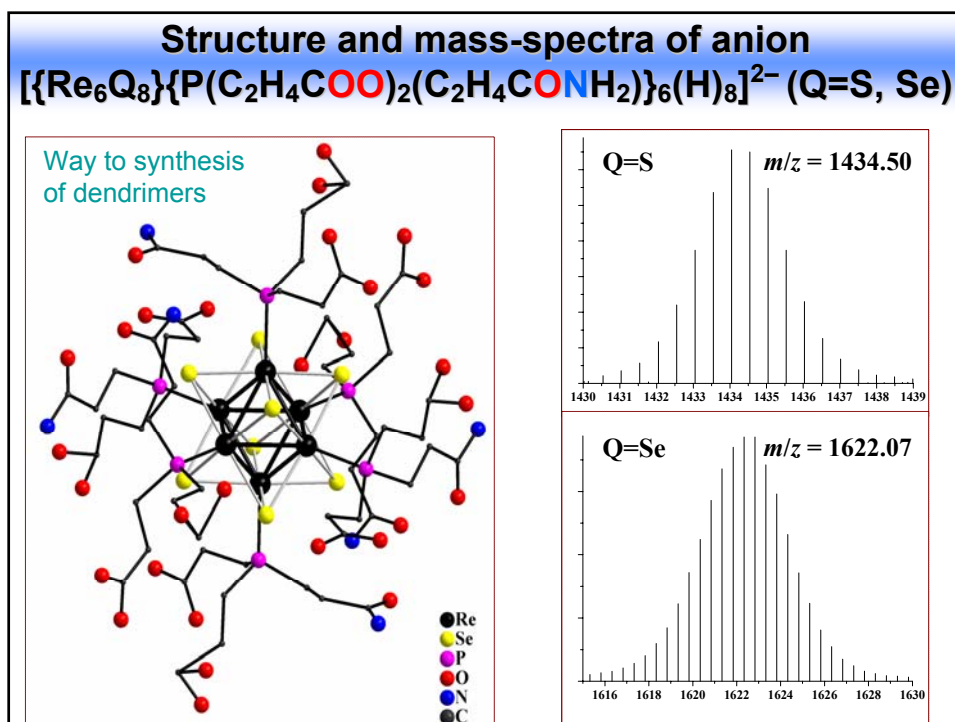
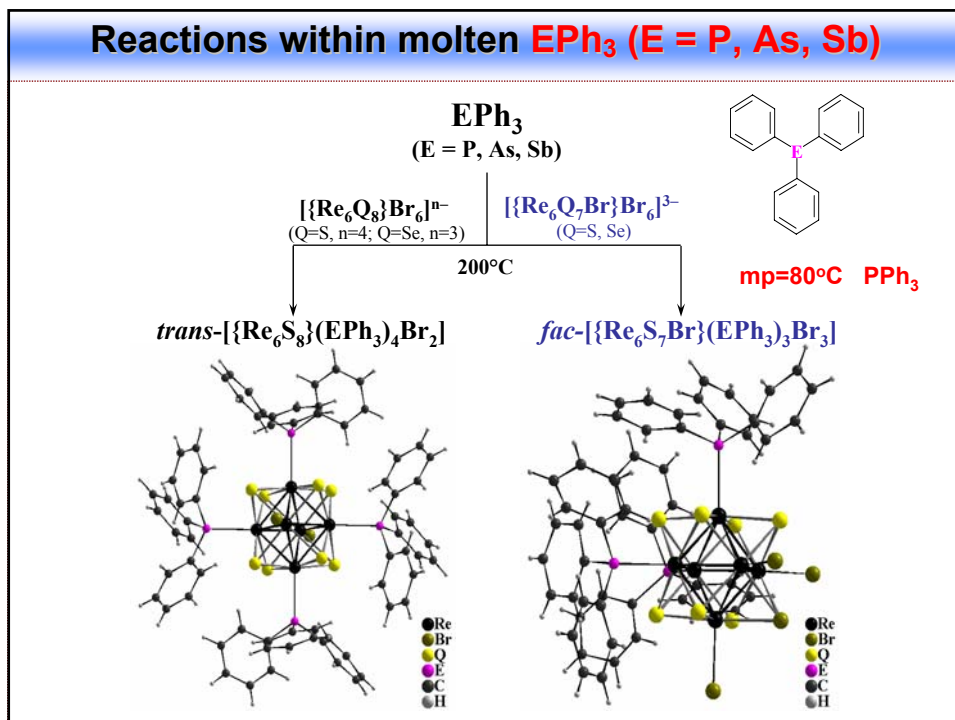


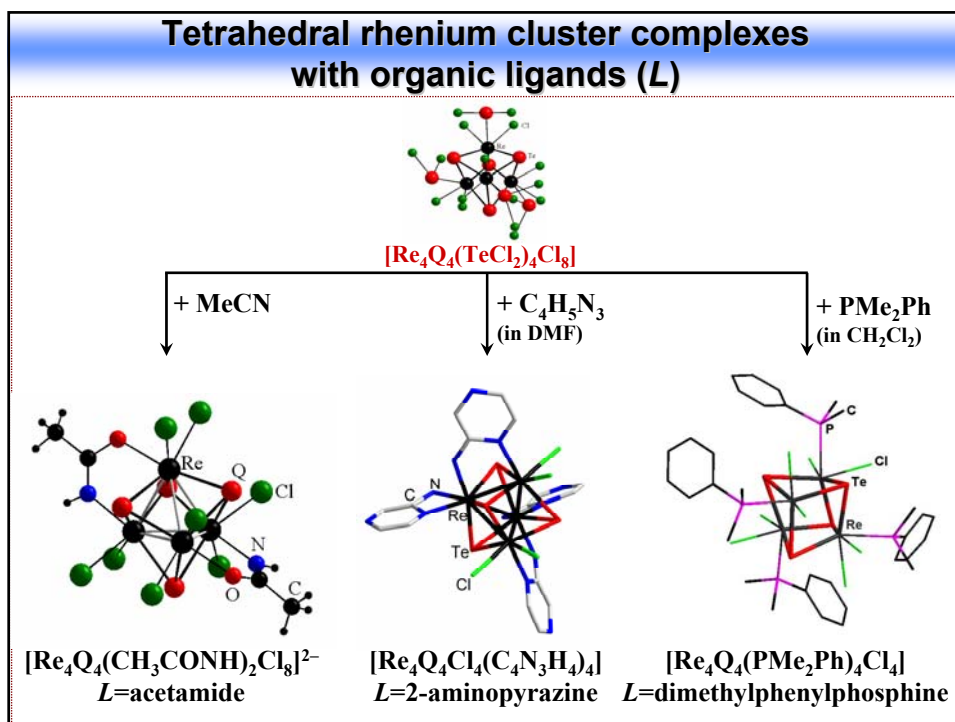
Influence of substitution of metal atoms in cluster core on luminescent properties of cluster complexes





Reactions within molten EPh_3 (E = P, As, Sb)





ACSCE

Acta Crystallographica Section C

Crystal Structure Communications

Vol. C52 Part 5 Pp. 1061–1318 15 May 1996

Re₄S₄Te₄, a tetrahedral cluster compound...

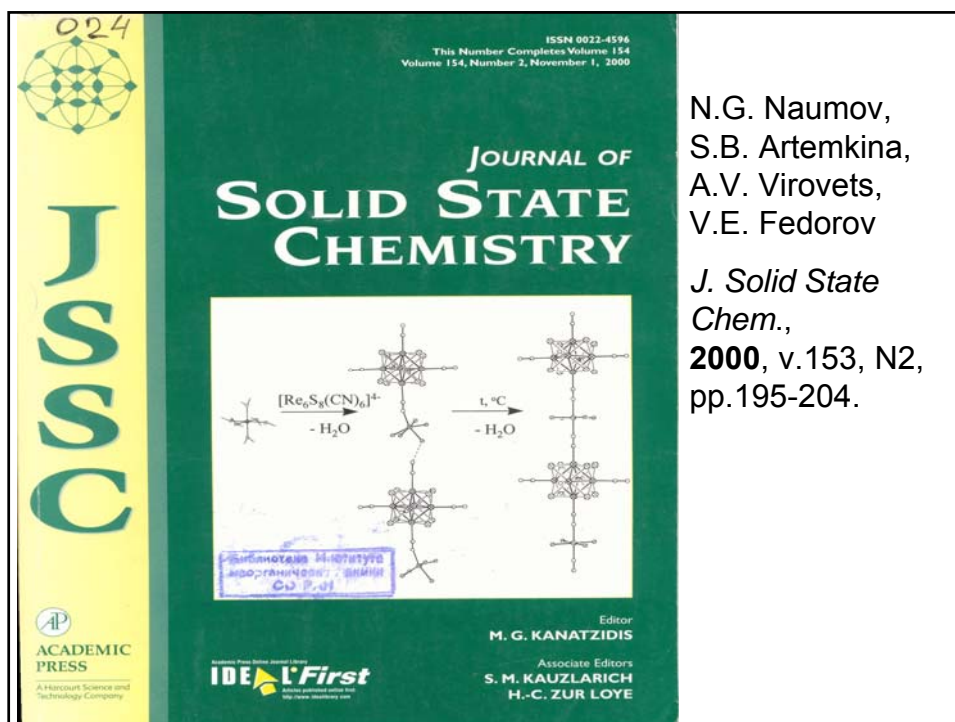
Editor: S. R. Hall

Published for the INTERNATIONAL UNION OF CRYSTALLOGRAPHY
by MUNKSGAARD, International Booksellers and Publishers Ltd, Copenhagen

V.E. Fedorov,
Yu.V. Mironov,
V.P. Fedin,
H. Imoto,
T. Saito

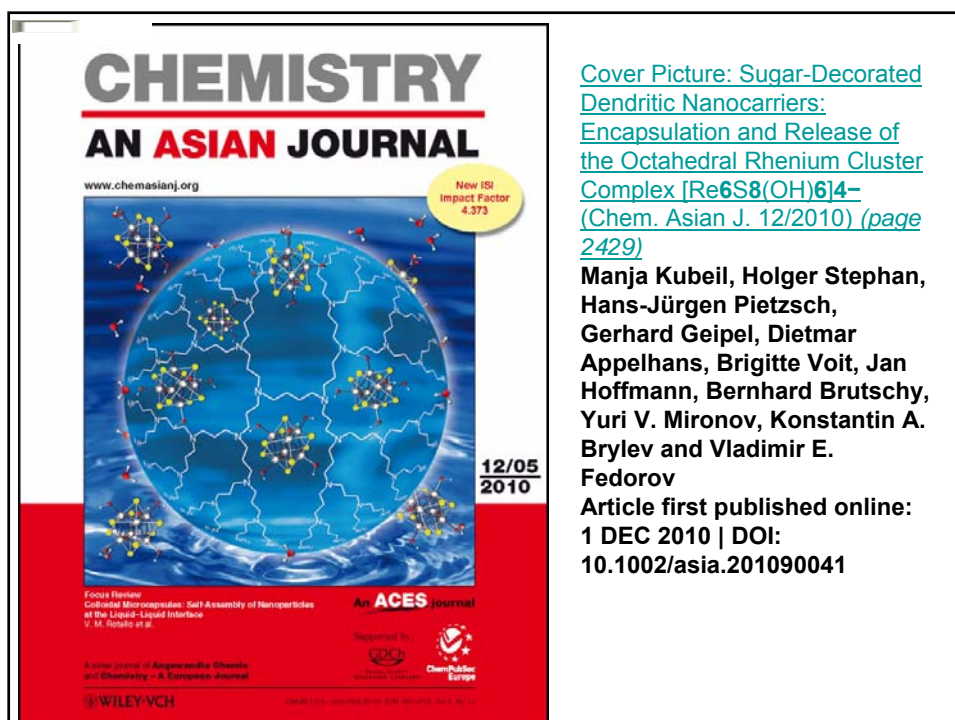
Re₄S₄Te₄

Acta Cryst., **1996**,
v.C52, pp.1065-
1067.



N.G. Naumov,
S.B. Artemkina,
A.V. Virovets,
V.E. Fedorov

J. Solid State Chem.,
2000, v.153, N2,
pp.195-204.

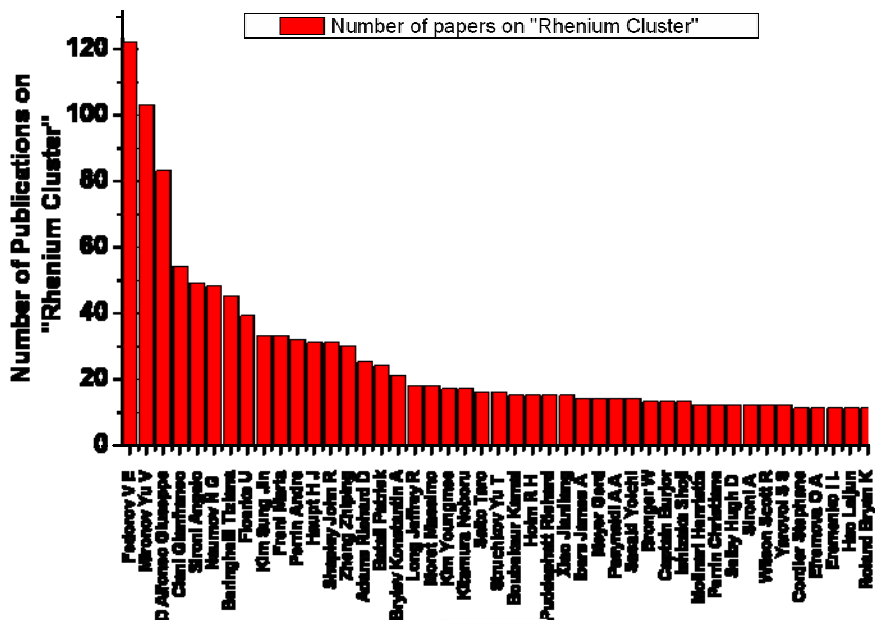


[Cover Picture: Sugar-Decorated Dendritic Nanocarriers: Encapsulation and Release of the Octahedral Rhenium Cluster Complex \[Re₆S₈\(OH\)₆\]⁴⁻ \(Chem. Asian J. 12/2010\) \(page 2429\)](#)

Manja Kubeil, Holger Stephan, Hans-Jürgen Pietzsch, Gerhard Geipel, Dietmar Appelhans, Brigitte Voit, Jan Hoffmann, Bernhard Brutschy, Yuri V. Mironov, Konstantin A. Brylev and Vladimir E. Fedorov

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**1 DEC 2010 | DOI:
10.1002/asia.201090041**

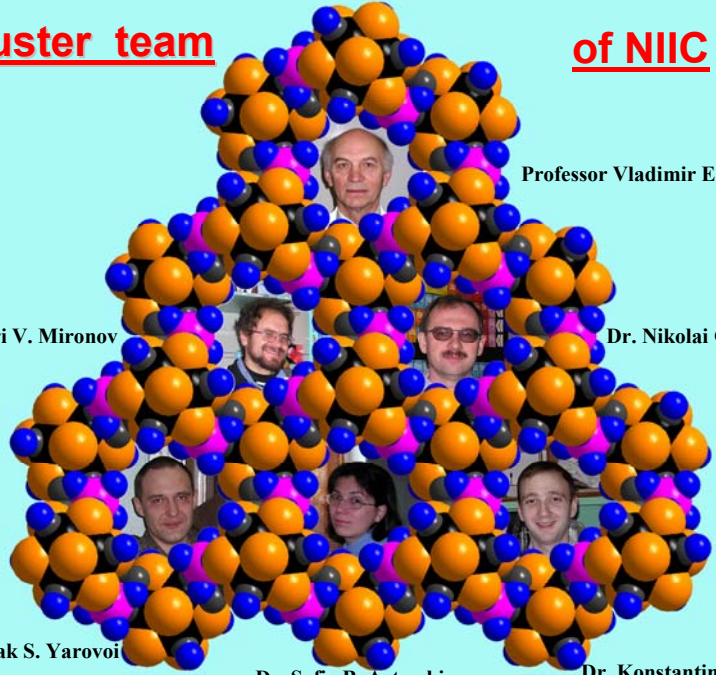
Our contribution to cluster science of rhenium



CONCLUSION:

- More than two hundreds of new complex cluster rhenium compounds are synthesized; some complexes playing key role in cluster chemistry of transition metals were discovered.
- Structures and properties of all compounds obtained were studied by a set of modern high informative methods.
- More than two hundreds articles including several reviews have been published in high level journals.
- 3 dissertations of Doctor of Chemical Sciences and 11 dissertations of Candidate of Chemical Sciences were prepared and defended successfully.
- Many reports including invited lectures were presented on different international scientific conferences.

Cluster team of NIIC



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Dr. Sofia B. Artemkina

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Stuttgart, Germany:
Prof. A. Simon

Evanston, USA:
Prof. J. Ibers

Seoul, Korea:
Prof. S.J. Kim

Sapporo, Japan:
Prof. N. Kitamura

Rennes, France:
Prof. A. Perrin
Dr. C. Perrin

Dresden, Germany:
Dr. H.-Ju. Pietsch

Bochum, Germany:
Prof. W.S. Sheldrick

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