7th International Symposium on Technetium and Rhenium Science and Utilization

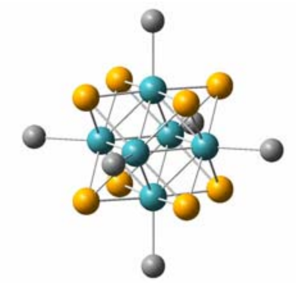
Spectroscopic and photophysical properties of chalcogenide-capped octahedral hexarhenium complexes with N-heteroaromatic ligands

Takashi Yoshimura

Department of Chemistry, Graduate School of Science, Osaka University

Plenary lecture

Octahedral Hexametal Complex



4	5	6	7	8	9
$_{22}$Ti Titanium	$_{23}$V Vanadium	$_{24}$Cr Chromium	$_{25}$Mn Manganese	$_{26}$Fe Iron	$_{27}$Co Cobalt
$_{40}$Zr Zirconium	$_{41}$Nb Niobium	$_{42}$Mo Molybdenum	$_{43}$Tc Technetium	$_{44}$Ru Ruthenium	$_{45}$Rh Rhodium
$_{72}$Hf Hafnium	$_{73}$Ta Tantalum	$_{74}$W Tungsten	$_{75}$Re Rhenium	$_{76}$Os Osmium	$_{77}$Ir Iridium

Metal ion

Chalcogenide or Halide

Donor (C, N, O, F, P, S, Cl, As, Se, Br, Sb, Te, I)
Terminal ligand

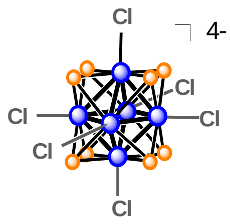
V. E. Fedorov, et al.

$Re_6Q_4X_{10}$ (Q = Se, Te; X = Cl, Br)

Russ. J. Inorg. Chem. **1971**, *16*, 790
Russ. J. Inorg. Chem. **1971**, *16*, 1685

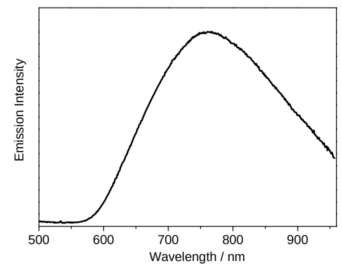
24 electron Complexes
Re_6(III,III,III,III,III,III)
⟶ Re_6(24e)
Structural Chemistry including Supramolecule
Redox Properties
Photoluminescent Properties

Photoluminescence of the Hexarhenium Complex



$[Re_6S_8Cl_6]^{4-}$

Emission Spectrum for $[Re_6S_8Cl_6]^{4-}$ in CH_3CN at 296 K



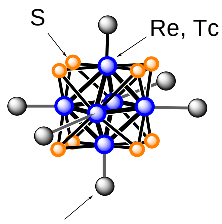
Spectroscopic and photophysical data in CH_3CN at 296 or 300 K

	λ_{em} / nm	Φ_{em}	τ_{em}/μs
$[Mo_6Cl_8Cl_6]^{2-}$, a	805	0.19	180
$[W_6Cl_8Cl_6]^{2-}$, a	880	0.02	2.2
$[Re_6S_8Cl_6]^{4-}$, b	770	0.039	6.3

a, H. B. Gray et al. *J. Am. Chem. Soc.* **1983**, *105*, 1878
b, T. Yoshimura et al. *Chem. Lett.* **1999**, 697
C. Guilbaud et al. *Chem. Commun.* **1999**, 1867
T. G. Gray et al. *Inorg. Chem.* **1999**, 38, 5932

This study

Sulfide-capped Hexarhenium Complexes with N-heteroaromatic Ligands

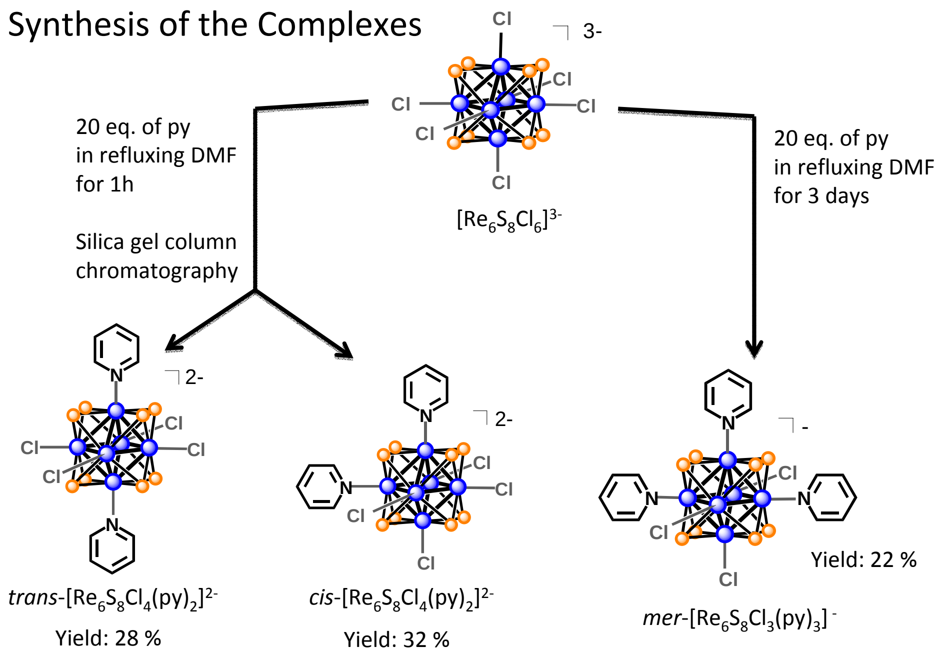


Synthesis of $[Re_6S_8Cl_{6-n}(pyridine)_n]^{n-4}$ (n = 1-3)
Redox Properties
Photoluminescent Properties

Chalcogenide-capped Hexatechnetium Complexes with Cyanide

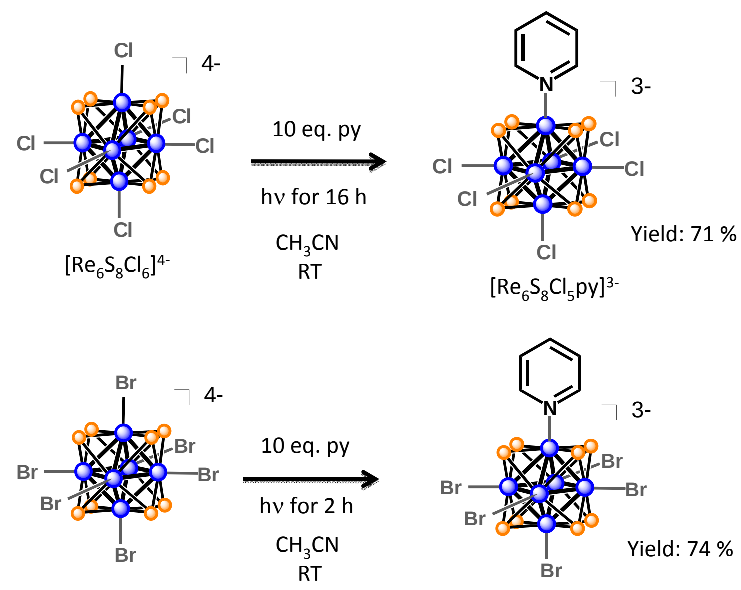
Synthesis of $[Tc_6S_8(CN)_6]^{4-}$ and $[Tc_6Se_8(CN)_6]^{4-}$
Redox Properties

Synthesis of the Complexes

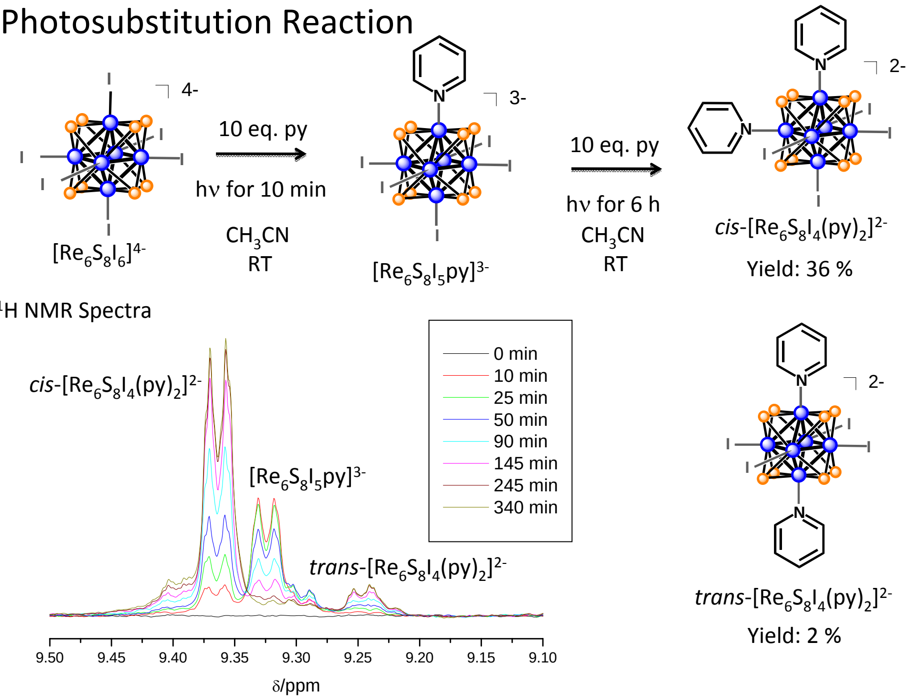


T. Yoshimura, et al. *Inorg. Chem.* **1999**, 5557
T. Yoshimura , et al. *Inorg. Chem.* **2000**, 1765

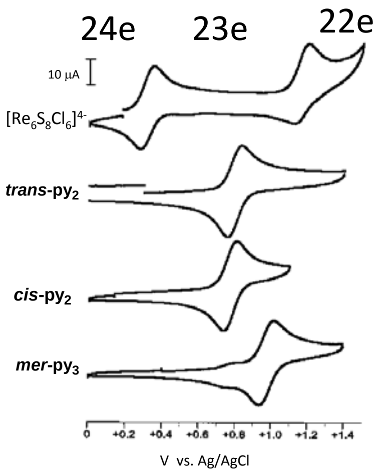
Photosubstitution Reaction
Synthesis of $[Re_6S_8X_5py]^{3-}$



Photosubstitution Reaction

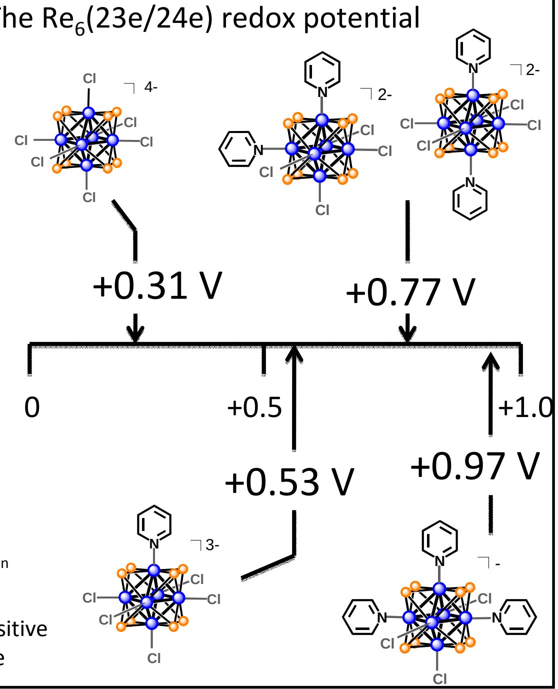


Redox Properties



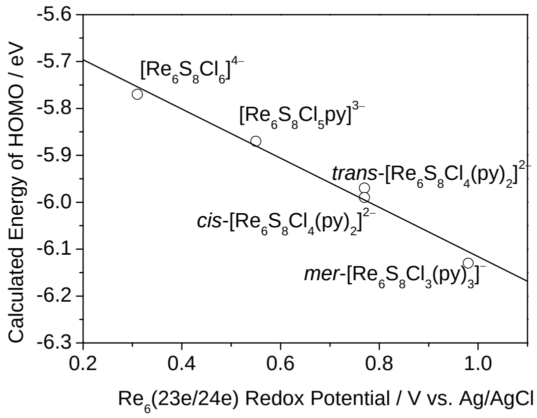
Cyclic Voltammograms in 0.1 M $(Bu_4N)PF_6$-CH_3CN solution

The Re_6(23e/24e) redox potential



The Re_6(23e/24e) potential shifts to positive along with substitution of Cl by pyridine

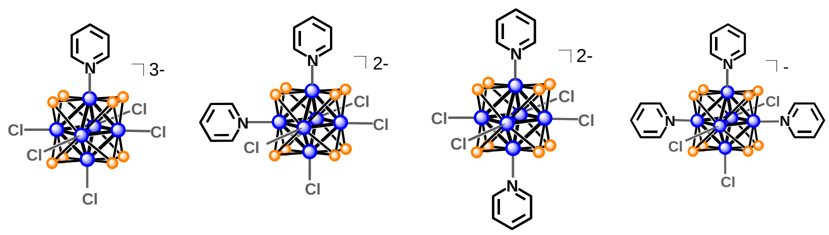
DFT Calculations (Gaussian 03 B3LYP/Lanl2dz)

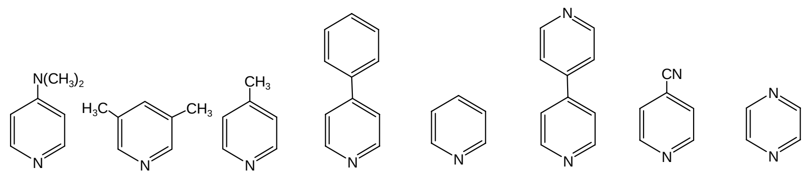


A linear correlation between the Re_6(23e/24e) potential and the energy level of HOMO

The positive shift of Re_6(23e/24e) redox potential according with substitution of Cl by py reflects the energy level of HOMO

Synthesis of $[Re_6S_8Cl_{6-n}(L)_n]^{n-4}$ complexes (L = pyridine derivatives)

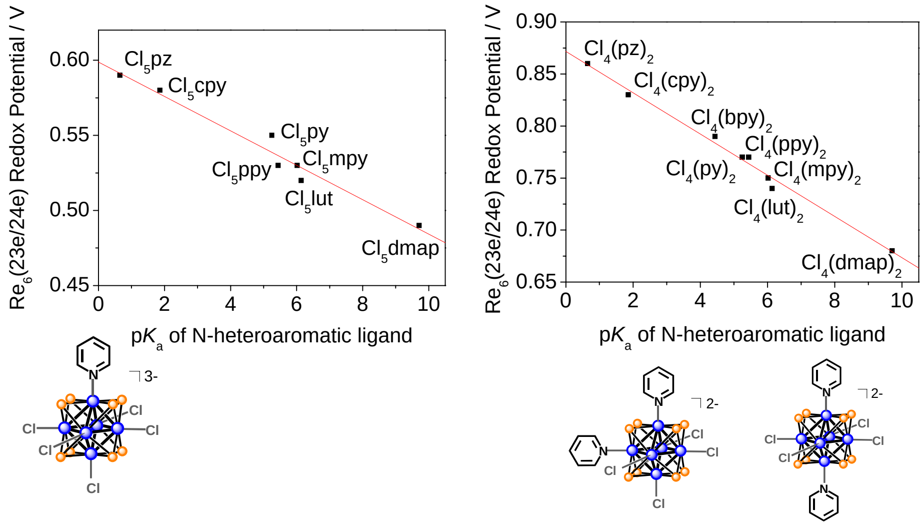




	dmap	lut	mpy	ppy	py	bpy	cpy	pz
pK_a	9.71	6.14	6.02	5.44	5.25	4.44	1.86	0.65
E_L / V	0.14	0.21	0.23	0.23	0.25	0.27	0.32	0.33

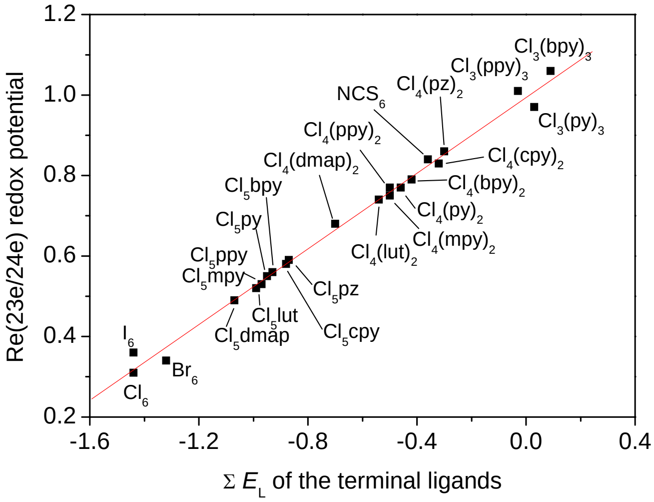
A. B. P. Lever, *Inorg. Chem.* **1990**, 1271

A correlation of pK_a of N-heteroaromatic ligand with the Re_6(23e/24e) redox potential



The donating ability of N-heteroaromatic ligand gives influence to the Re_6(23e/24e) Potential

A Plot of Re_6(23e/24e) redox potentials against E_L values of the terminal ligands

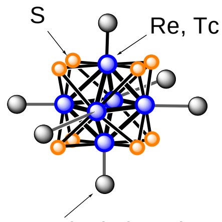


The Re_6(23e/24e) potential was controlled by the number and combination of the terminal halides and N-heteroaromatic ligands

This study

Sulfide-capped Hexarhenium Complexes with Pyridine-type Ligands

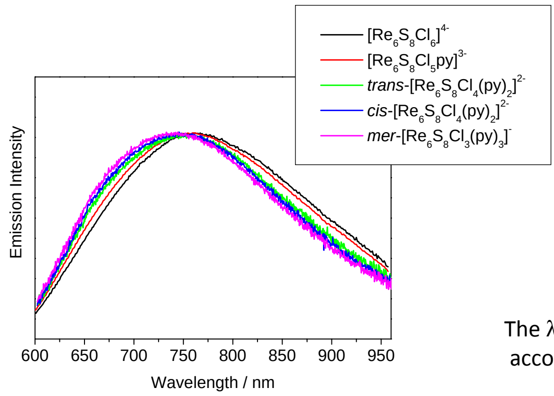
Synthesis of $[Re_6S_8Cl_{6-n}(pyridine)_n]^{n-4}$ (n = 1-3)
Redox Properties
Photoluminescent Properties



Chalcogenide-capped Hexatechnetium Complexes with Cyanide

Synthesis of $[Tc_6S_8(CN)_6]^{4-}$ and $[Tc_6Se_8(CN)_6]^{4-}$
Redox Properties

Spectroscopic and Photophysical Properties of $[Re_6S_8Cl_{6-n}(py)_n]^{n-4}$ (n =0-3)



- A broad emission spectral shape
- The lifetime of several μs
- Small or no solvent dependence of emission spectrum

Re_6 core-centered excited state

The λ_{em} value is shift to shorter wavelength according with substitution of Cl by pyridine

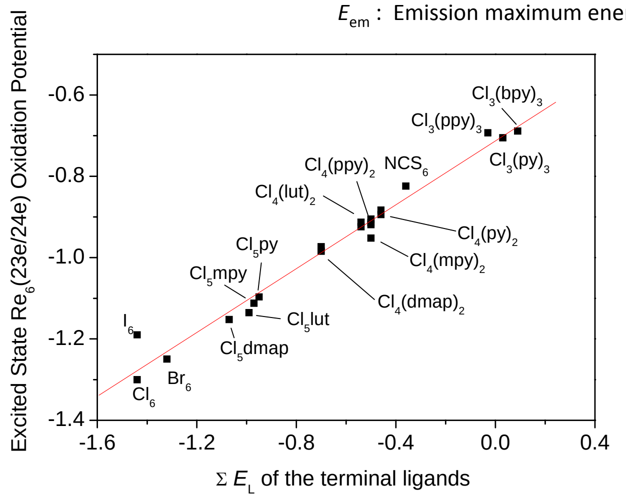
Spectroscopic and photophysical data of $[Re_6S_8Cl_{6-n}(py)_n]^{n-4}$ (n = 0 - 3) in CH_3CN at 296 K

Complex	λ_{em} / nm	Φ_{em}	τ_{em} / μs
$[Re_6S_8Cl_6]^{4-}$	770	0.039	6.3
$[Re_6S_8Cl_5py]^{3-}$	756	0.040	4.6
trans-$[Re_6S_8Cl_4(py)_2]^{2-}$	750	0.033	4.5
cis-$[Re_6S_8Cl_4(py)_2]^{2-}$	745	0.042	5.1
mer-$[Re_6S_8Cl_3(py)_3]^{-}$	740	0.045	5.9

Oxidation Potentials of the Excited Complexes

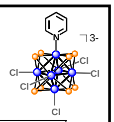
$$E^*_{ox} = E_{ox} - E_{em}$$

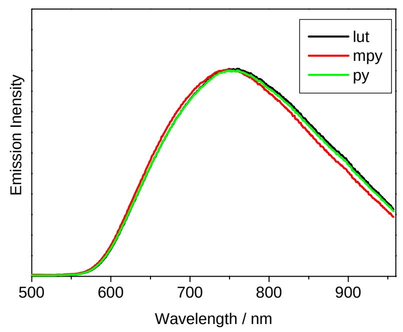
E^*_{ox} : oxidation potential in the excited state
E_{ox} : oxidation potential in the ground state
E_{em} : Emission maximum energy



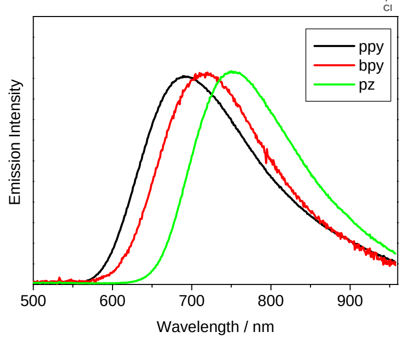
A linear correlation between sum of E_L values of the terminal ligands and the Re_6(23e/24e) oxidation potentials at the excited state

N-heteroaromatic Ligand Dependence of Spectroscopic and Photophysical Properties





Emission spectra in the solid state at 296 K



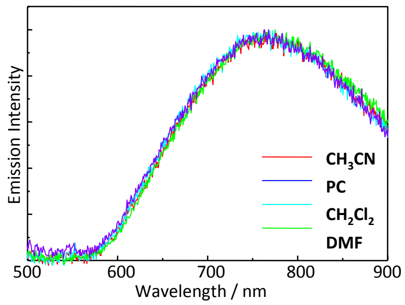
Emission spectra in the solid state at 296 K

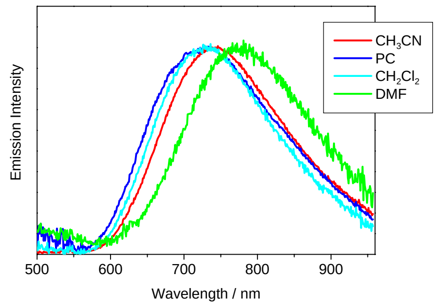
Spectroscopic and photophysical data in CH_3CN at 296 K

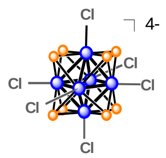
	λ_{em} / nm	Φ_{em}	τ_{em}/µs
$[Re_6S_8Cl_5lut]^{3-}$	756	0.046	5.9
$[Re_6S_8Cl_5mpy]^{3-}$	755	0.022	4.9
$[Re_6S_8Cl_5py]^{3-}$	756	0.040	4.6

	λ_{em} / nm	Φ_{em}	τ_{em}/µs
$[Re_6S_8Cl_5ppy]^{3-}$	739	0.0089	0.33
$[Re_6S_8Cl_5bpy]^{3}$	No luminescence		
$[Re_6S_8Cl_5pz]^{3-}$	No luminescence		

Solvent Dependence of Spectroscopic and Photophysical Properties



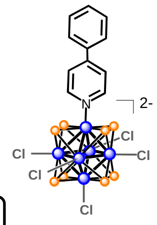




$[Re_6S_8Cl_6]^{4-}$

No solvent dependence of Emission spectra

Re$_6$ Core-centered excited state

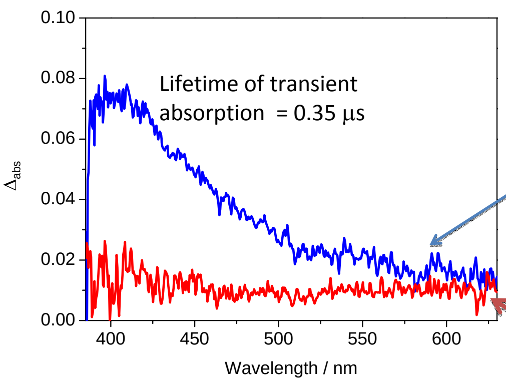


$[Re_6S_8Cl_5ppy]^{3-}$

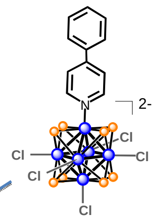
Large solvent dependence of Emission spectra

Excited state character is different from the Re$_6$ core-centered type

Transient Absorption Spectra of $[Re_6S_8Cl_5ppy]^{2-}$ and $[Re_6S_8Cl_6]^{4-}$ in CH_3CN at 296 K



Transient absorption spectra of $(Bu_4N)_3[Re_6S_8Cl_5ppy]$ (blue) and $(Bu_4N)_4[Re_6S_8Cl_6]$ (red) in CH_3CN at 296 K.

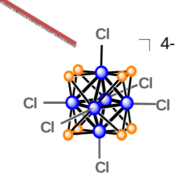


$[Re_6S_8Cl_5ppy]^{3-}$

Emission lifetime = 0.33 μs

Transient absorption spectra is similar to that of ppy$^-$ anion

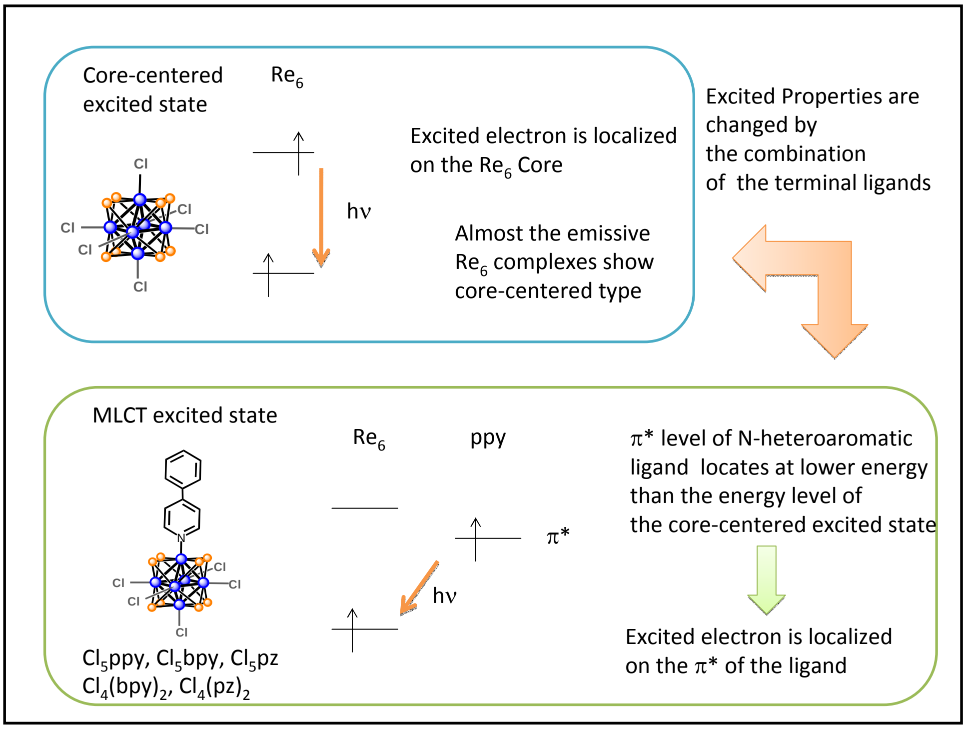
Re$_6$-to-ppy MLCT excited state



$[Re_6S_8Cl_6]^{4-}$

Excitation at 355 nm
Probe light: Xenon Lamp

No intense transient absorption



Summary of Sulfide-capped Hexarhenium Complexes with N-heteroaromatic Ligands

Synthesis of the Complexes

The reaction of $[Re_6S_8Cl_6]^{3-}$ with excess amount of N-heteroaromatic ligand in refluxing DMF gave *trans*-, *cis*-$[Re_6S_8Cl_4$(N-heteroaromatic ligand)$_2]^{2-}$ and *mer*-$[Re_6S_8Cl_3$(N-heteroaromatic ligand)$_3]^{-}$. The photoirradiation of $[Re_6S_8Cl_6]^{4-}$ with excess amount of N-heteroaromatic ligand in CH_3CN at RT afforded $[Re_6S_8Cl_5$(N-heteroaromatic ligand)$]^{3-}$.

Electrochemical Properties

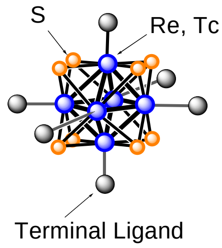
The Re_6(23e/24e) process at the ground and excited state were controlled by the donating ability of the N-heteroaromatic ligand and the number and combination of chloride and N-heteroaromatic Ligands

Spectroscopic and Photophysical Prperties

The complexes showed Re_6 core-centered or MLCT character in the excited state. The complex with low-lying π* orbital showed MLCT excited state.

This study

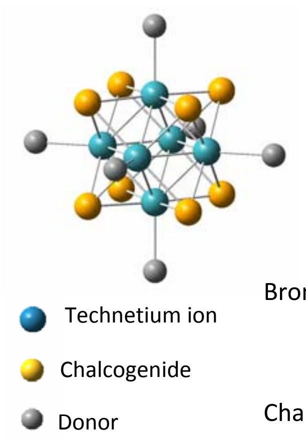
Sulfide-capped Hexarhenium Complexes with Pyridine-type Ligands



Synthesis of $[Re_6S_8Cl_{6-n}(pyridine)_n]^{n-4}$ (n = 1-3)
Redox Properties
Photoluminescent Properties

Chalcogenide-capped Hexatechnetium Complexes with Cyanide

Synthesis of $[Tc_6S_8(CN)_6]^{4-}$ and $[Tc_6Se_8(CN)_6]^{4-}$
Redox Properties



4	5	6	7	8	9
$_{22}$Ti Titanium	$_{23}$V Vanadium	$_{24}$Cr Chromium	$_{25}$Mn Manganese	$_{26}$Fe Iron	$_{27}$Co Cobalt
$_{40}$Zr Zirconium	$_{41}$Nb Niobium	$_{42}$Mo Molybdenum	$_{43}$Tc Technetium	$_{44}$Ru Ruthenium	$_{45}$Rh Rhodium
$_{72}$Hf Hafnium	$_{73}$Ta Tantalum	$_{74}$W Tungsten	$_{75}$Re Rhenium	$_{76}$Os Osmium	$_{77}$Ir Iridium

Bromide Capped Hexatechnetium Complex
$[Tc_6(\mu_3\text{-}Br)_5Br_6]^{2-}$
S. V. Kryutchkov et al., *Z. Anorg. Allg. Chem.*, **1988**

Chalcogenide Capped Hexatechnetium Complex
Tc_6S_{14}, Tc_6S_{12}, Tc_6Se_{12}
W. Bronger et al., *Angew. Chem.*, **1993**, *Z. Anorg. Allg. Chem.*, **1993**

$[Tc_6S_8X_6]^{4-}$ (X = Br, I), $[Tc_6Se_8Br_4]^{2-}$, $Tc_6Se_8I_2$, and Tc_6Te_{15}
T. Yoshimura et al. *Eur. J. Inorg. Chem.* **2010**, 1214.

Octahedral Hexatechnetium Complexes with Cyanide
Synthesis, Structures, Redox Properties and Electronic Structures

Hexarhenium Complex with Cyanide

Y. V. Mironov et al.

$$Re_6Te_{15} \xrightarrow[500\ ^oC\ \text{for 24 h}]{KSCN} [Re_6S_8(CN)_6]^{4-}$$

Croat. Chem. Acta **1995**, 885

$$Re_6Te_{15} \xrightarrow[600\ ^oC\ \text{for 24 h}]{Se,\ NaCN} [Re_6Se_8(CN)_6]^{4-}$$

$$Re_6Te_{15} \xrightarrow[600\ ^oC\ \text{for 24 h}]{NaCN} [Re_6Te_8(CN)_6]^{4-}$$

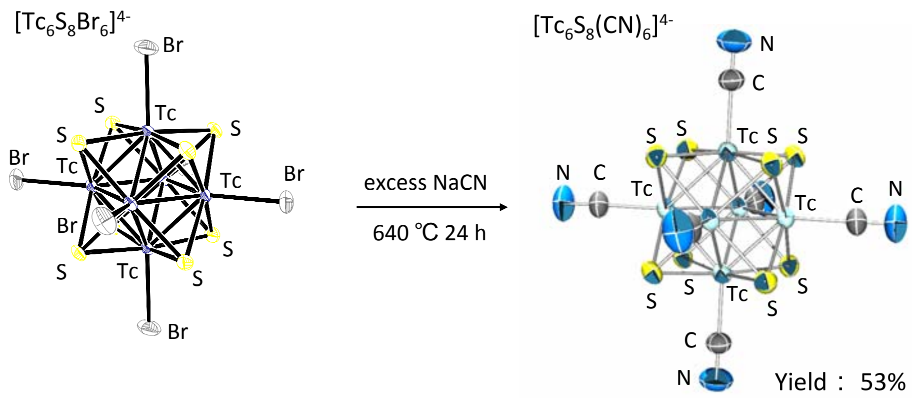
J. Am. Chem. Soc. **1997**, 493

J. R. Long et al.

$$[Re_6Q_8X_6]^{4-} \xrightarrow[635\ ^oC\ \text{for 25 h}]{NaCN} [Re_6Q_8(CN)_6]^{4-} \quad (Q = S, Se)$$

Chem. Mater. **1998**, 3783

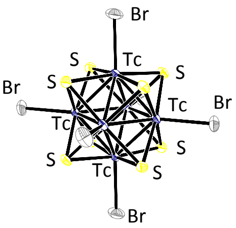
Reaction of $[Tc_6S_8Br_6]^{4-}$ with NaCN

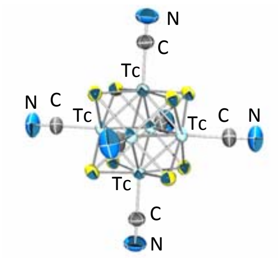


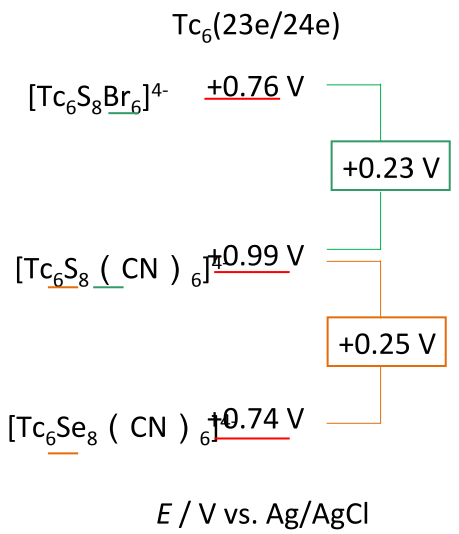
IR (KBr, ν, cm^{-1}) : 2114

T. Yoshimura et al. *Inorg. Chem.* **2010**, *49*, 5876.

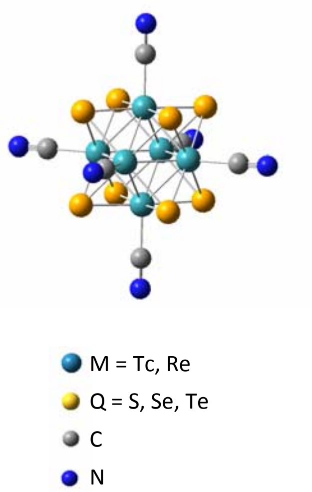
Redox Properties of the Hexatechnetium Complexes

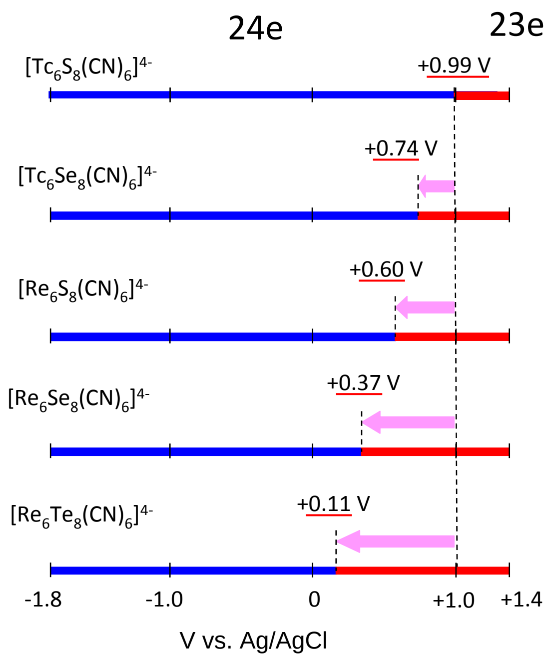




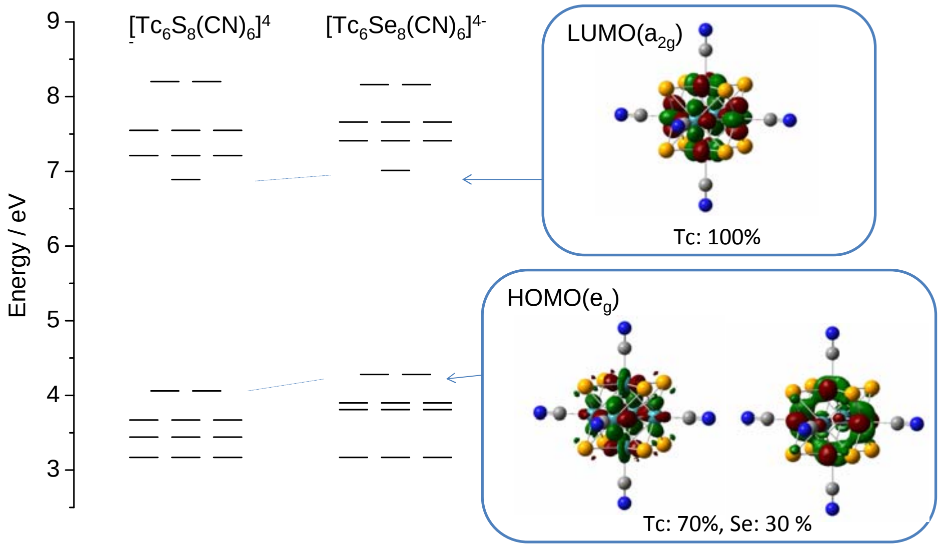


Dependence of Redox Potential in $[M_6(m_3\text{-}Q)_8(CN)_6]^{4-}$ (M = Tc, Re; Q = S, Se, Te)



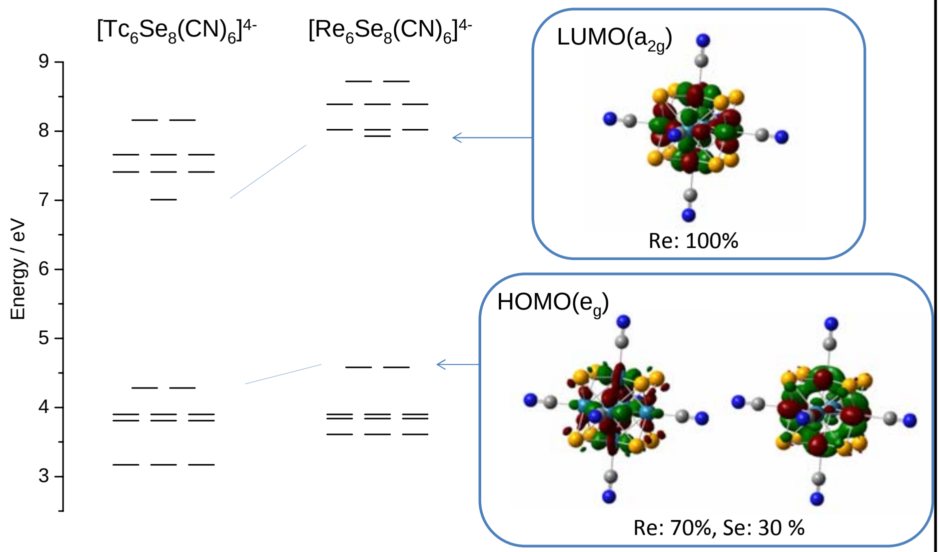


Energy Level Diagrams of the Hexatechnetium(III) Complexes (DFT calculation B3LYP/LanL2dz)



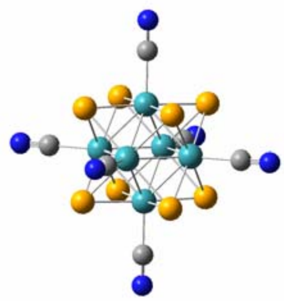
The energy level of HOMO is stabilized in the sulfide complex compared with the selenide complex

Energy Level Diagrams of the Hexatechnetium(III) and Hexarhenium(III) Complexes

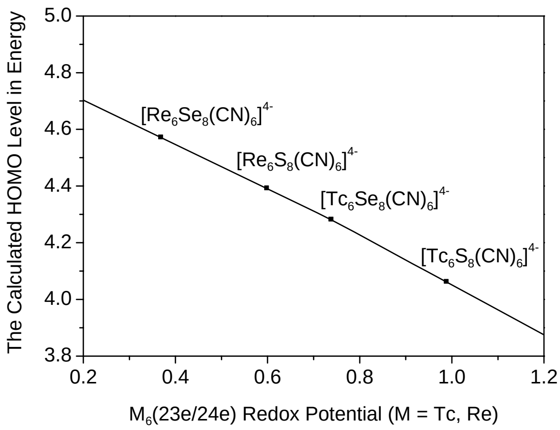


The energy level of HOMO is stabilized in the technetium complex compared with the rhenium analog

Plot of Energy Level of HOMO against the redox potential of M_6(23e/24e)

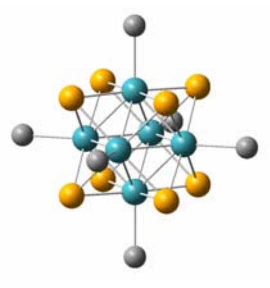


- M = Tc, Re
- Q = S, Se
- C
- N



The M_6(23e/24e) redox potentials reflect the energy level of HOMO

Summary of Octahedral Hexatechnetium Complexes with Cyanide



- Tc
- Chalcogenide
- Br, CN, I, Te, NCS

Structure

Bond distances and angles of Tc_6 complexes resemble those of Re_6 analogues

Redox Properties

The Tc_6(23e/24e) redox process occurred at more positive potential than the Re_6(23e/24e) In the Re analog.

Electronic Structure of Tc_6 Complex

The HOMO and LUMO energy levels in the Tc_6 complex were more stabilized compared with those in the Re_6 analog.

The HOMO-LUMO energy gap of the Tc_6 complex was smaller than that of the Re_6 analog.

T. Yoshimura et al. *Eur. J. Inorg. Chem.* **2010**, 1214.

T. Yoshimura et al. *Inorg. Chem.* **2010**, *49*, 5876.

Acknowledgement

Osaka Univ.
- A. Shinohara
- T. Ikai
- C. Suo

Tohoku Univ.
- T. Sekine
- Y. Kino
- N. Sato
- A. Kirishima

Daido Univ.
- T. Takayama

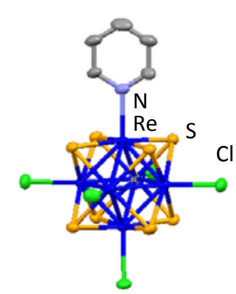
Toyama Univ.
- K. Tsuge
- K. Nozaki

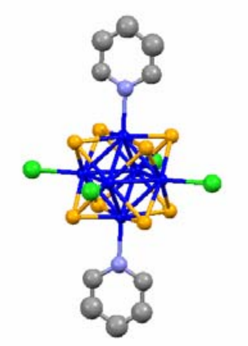
Hokkaido Univ.
- N. Kitamura
- Y. Sasaki
- S. Ishizaka
- E. Sakuda
- A. Ito
- T. Kashiwa

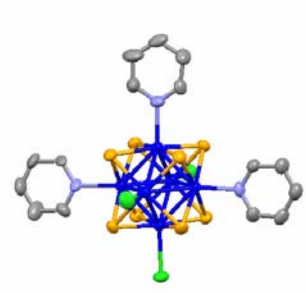
Nagasaki Univ.
- K. Umakoshi

Kyushu Univ.
- M. Abe

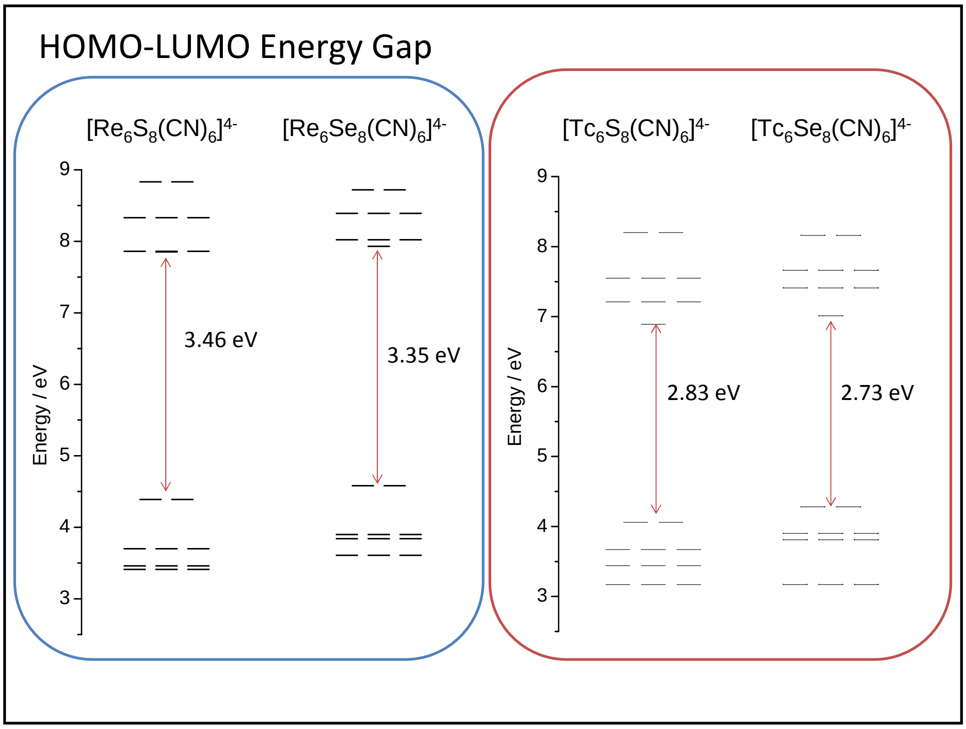
X-ray Structures







	$[Re_6S_8Cl_5py]^{3-}$	*trans*-$[Re_6S_8Cl_4(py)_2]^{2-}$	*mer*-$[Re_6S_8Cl_3(py)_3]^{-}$
Re-Re/ Å	av. 2.594(1)	av. 2.593(1)	av. 2.594(1)
Re-Cl / Å	av. 2.435(5)	av. 2.427(3)	av. 2.424(7)
Re-S / Å	av. 2.40(1)	av. 2.40(1)	av. 2.40(1)
Re-N / Å	2.191(6)	2.18(1)	2.19(2)



HOMO-LUMO Energy Gap
[Re6S8(CN)6]4-
[Re6Se8(CN)6]4-
[Tc6S8(CN)6]4-
[Tc6Se8(CN)6]4-
Energy / eV
3.46 eV
3.35 eV
2.83 eV
2.73 eV