STEM Scholars Program 2015

Keggin Polyoxometalate incorporating $(TcX)^{3+}$cores Where X=N,O

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Introduction

Technetium-99 (^{99}Tc) is an isotope of technetium which decays with a half-life of 213,000 years to stable ruthenium-99, emitting beta particles[1], but no gamma rays. It is the most significant long-lived fission product of uranium fission, producing the largest fraction of the total long-lived radiation emissions of nuclear waste. Technetium-99 has a product yield of 6.0507% for thermal neutron fission of uranium-235.

Properties of Technetium

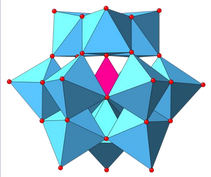
- Exists as only radioactive isotopes.
- 99Tc long half life (t1/2= 2.13 x 105 years).
- Complex redox chemistry (-1 to +7).
- Tc in the +7 oxidation state is mobile in the environment.

Research Aim

- Study the chemistry of ^{99}Tc in metal oxide storage matrices using Polyoxometalates (POMs) as metal oxide mimics.
- Tc in the +7 oxidation state is mobile in the environment. We need to find a way to stabilize it in a lower oxidation state.

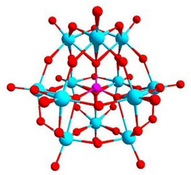
Polyoxometalates

- Polyatomic ions, usually an anion.
- Transition metal oxide clusters (Different formation).
- Metal oxyanions linked together by shared oxygen atoms to form a large, closed 3-dimensional framework.



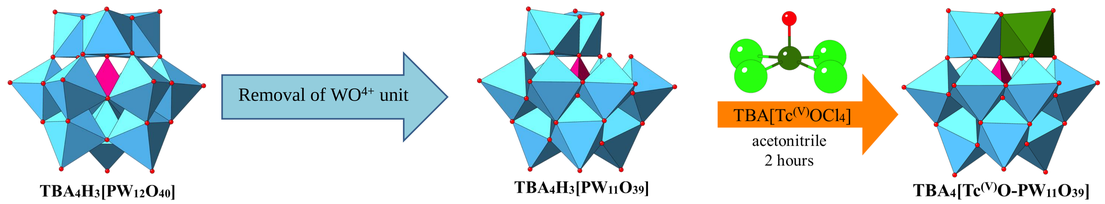
Polyhedral Representation

The Keggin POM $[PW_{12}O_{40}]^{-3}$



Ball and Stick Representation

Synthesis of complexes ($Tc^{V}O$)



- Metal will be incorporated into a defect site.
- Hard metal ions can incorporate into these defects. i.e. higher valent $Tc^{V} - Tc^{VII}$

Results

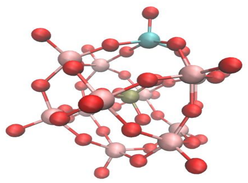
Computational Results

System	Energy (HOMO/ev)	Energy (LUMO/ev)	Band Gap/ev
TcO	4.136	4.979	0.843
TcN	3.808	4.326	0.518

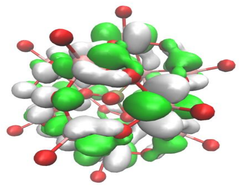
Orbitals Composition

System	HOMO	LUMO	LUMO +1	LUMO +2
TcO	52% Tc-d	54% Tc-d 21% O-p	54% Tc-d 21% O-p	10% W-d
TcN	52% Tc-d	52% Tc-d	22% W-d	20% W-d

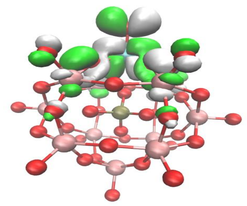
Structures



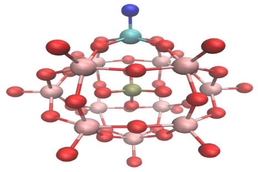
The Keggin POM $[PTcW_{11}O_{40}]^{-4}$



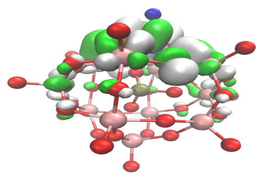
The Keggin POM $[PTcW_{11}O_{40}]^{-4}$ (HOMO)



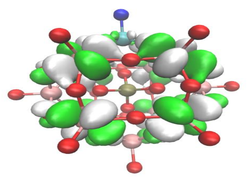
The Keggin POM $[PTcW_{11}O_{40}]^{-3}$ (LUMO)



The Keggin POM $[PTcW_{11}O_{39}\ N]^{-4}$



The Keggin POM $[PTcW_{11}O_{39}\ N]^{-4}$ (HOMO)



The Keggin POM $[PTcW_{11}O_{39}\ N]^{-3}$ (LUMO)

Electronic Structure Calculation

- Method – Local density spin approximation (LDSA)
- Basis set – metal lanl2tz(f), non-metal – 6-311g (p,d)
- Full geometry optimization with analytical gradients.
- Molecular Orbitals obtained for optimized structures.

Molecular Orbtial Calculations

- Band gap = Energy difference between the lowest unoccupied (LOMO) MO and the highest occupied (HOMO).
- Reactivity – As the band gap increases the systems is more reactive.

References

1. http://www-nds.iaea.org/sgnucdat/c3.htm Cumulative Fission Yields, IAEA.
2. The Structure and Formula of 12-Phosphotungstic Acid J.F. Keggin. Proc. Roy. Soc., A, 144, 851, 75-100 (1934) doi:10.1098/rspa.1934.0035.
3. From Scheele and Berzelius to Müller: polyoxometalates (POMs) revisited and the "missing link" between the bottom up and top down approaches P. Gouzerh, M. Che; L'Actualité Chimique, 2006, 298, 9.

Acknowledgement

Thanks to the STEM Scholars Program, Dr. Benjamin Burton-Pye from Hunter College, Professor Neal Phillip from BCC and Assistant Dean Felix Cardona from Hostos.