

Complexants for Actinide Element Coordination and Immobilization

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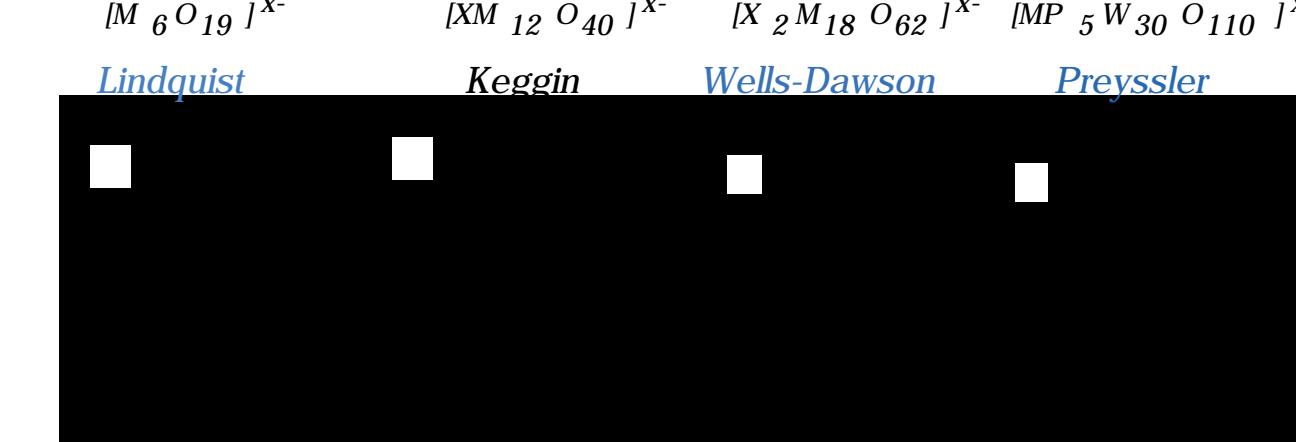
C O N C E P T

Use polyoxoanions (POAs) as complexants for the separation and immobilization of actinide ions from radioactive waste.

POLYOXOANIONS

- What are they?
 - Anionic, metal-oxide clusters, $[M_xO_y]^{2-}$ and $[X_aM_bO_c]^{d-}$, for $M = V, Nb, Mo, W$ and $X = Si, P$
 - Magic clusters:
 - discrete size
 - discrete structure
 - Form stable complexes with $4f/5f$ -ions
 - Electroactive, multi-electron oxidants: turn blue upon reduction, e⁻-delocalized in M-O band

POLYOXOANION STRUCTURES



Why Polyoxoanions?

They are robust, inexpensive, inorganic materials.
Technological uses in industrial catalysis.
Their physical properties can be tailored.

Objectives:

Develop stable and selective complexes of R ions.
Develop complexes that can be incorporated directly into wasteglass forms.

Technological Uses

Many Applications

Industrial Catalysis

Heterogeneous & homogeneous
N Acid catalyst

Isobutene → t-butyl alcohol

N Oxidation catalyst
Methacrolein → methacrylic acid

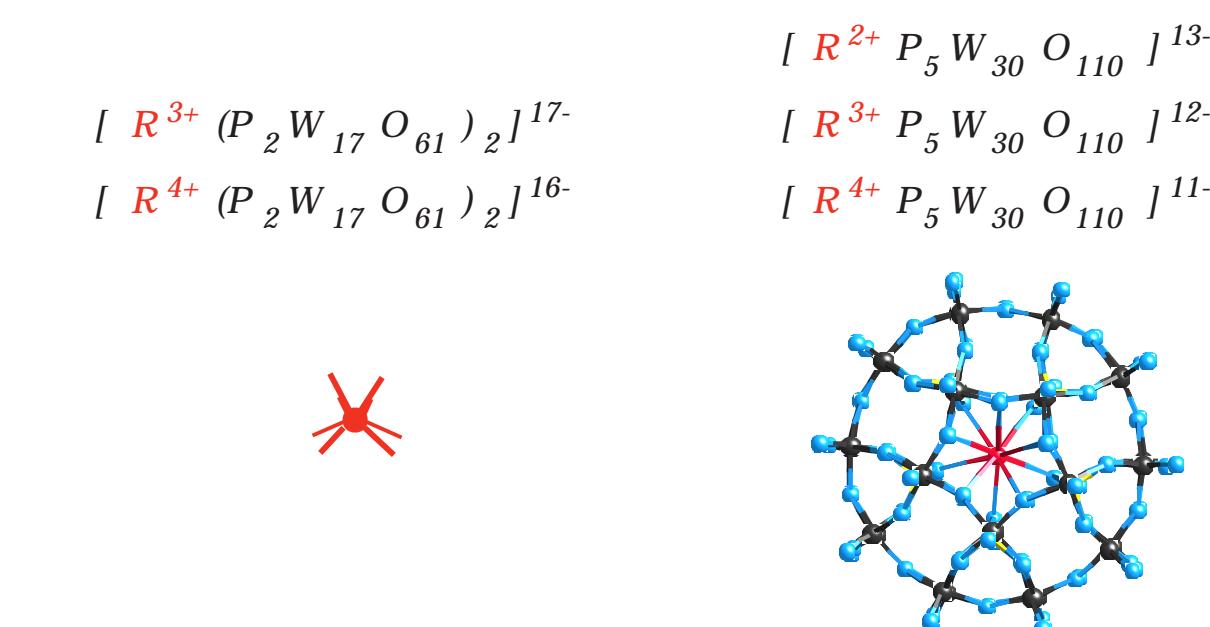
* D. Katsoulls, Chem. Rev. 1998, 98, 359.

* N. Mizuno, M. Misawa, J. Mol. Catal. 1994, 86, 319.

POLYOXOANION CHEMISTRY

- Easy and inexpensive to make.
- Soluble in aqueous and organic media
- Properties that impact reactivity with f-ions can be tailored: acidity, shape, size, polarity, ionic charge, redox potentials, surface charge distribution, etc.
- Thermal and oxidative stability. A. Savrykin, V. Spivayn, M. Orlova, O. Zhuravka, N. Krot, Radobelen, Engl Transl. 20, 1978, 207.
- Isolation of POAs in glasses. Precedence from sol-gel processing. A. Cherevko, J. Non-Cryst. Solids 147/148 (1992) 313.

Coordinate R (4f/5f) ions



STRATEGIC ISSUE

R-POA complexes have two redox centers:

1. R ion,
2. P-M-O framework.

R-POA redox chemistry is pivotal to exploitation of POAs as complexants for R ions in HLW processing.

A P P R O A C H

Synthesis

Electrochemistry

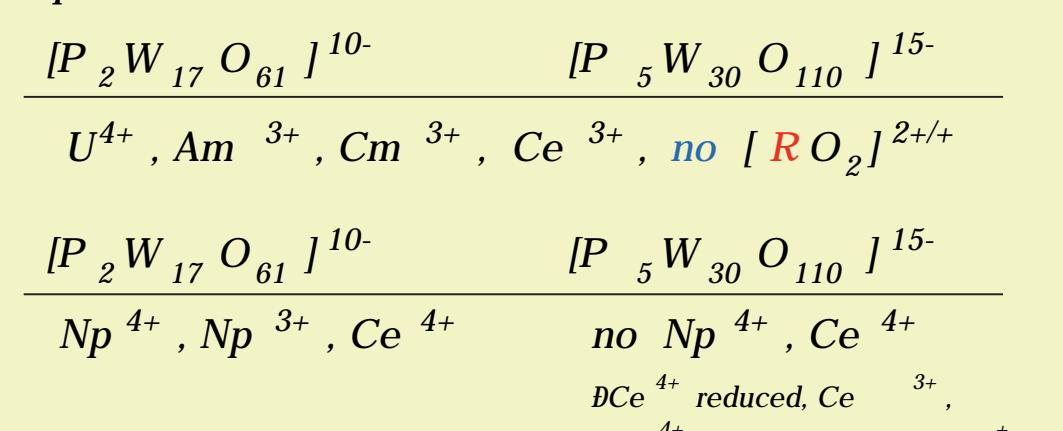
XAFS, X-ray Absorption Fine Structure

SAXS, Small Angle X-ray Scattering

Optical, NMR Spectroscopy

S U M M A R Y

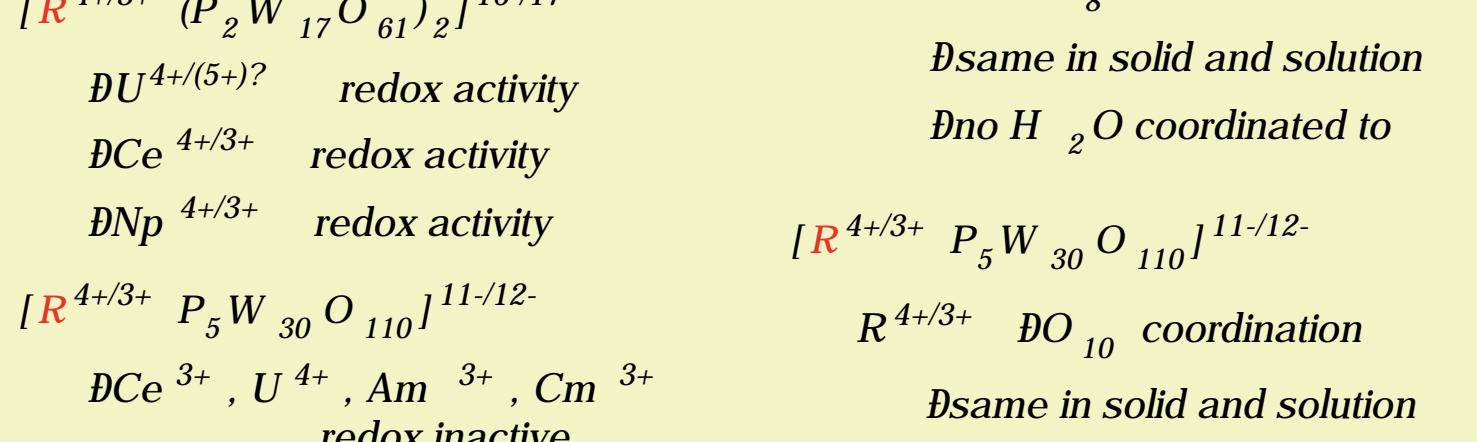
Binding of R ions by POAs depends upon R valence.



High-valent R complexes with $[Nb_6O_{19}]^{8-}$
Acid and base tolerant POAs

Electrochemistry

Reactions with high-valent R



$[R^{7+}/6+] [Nb_6O_{19}]^{8-}$
Under investigation

R Coordination

Reactions with R

Same in solid and solution

$DnO H_2O$ coordinated to R

$[R^{4+}P_5W_{30}O_{110}]^{11-12-}$

$R^{4+}/3+$ DO_{10} coordination

Same in solid and solution

$DnO H_2O$ coordination in channel

$[R^{7+}/6+] [Nb_6O_{19}]^{8-}$

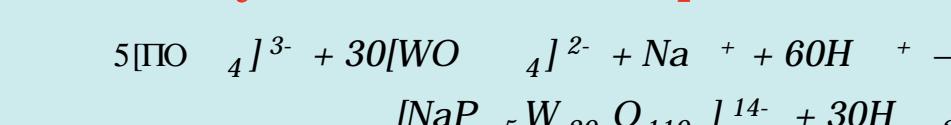
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FIRST RESULTS

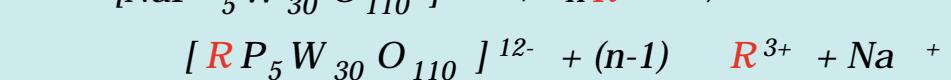
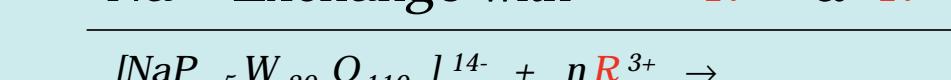
- R -POA redox behavior
- R -POA coordination
- R -POA glass chemistry

SYNTHESIS

R-Preussler Anion Complexes



Na^+ -Exchange with R^{3+} & R^{4+}



20-90 h, 160-240°C in Teflon vessel, $n = 1$ or 2. Yields ~90%

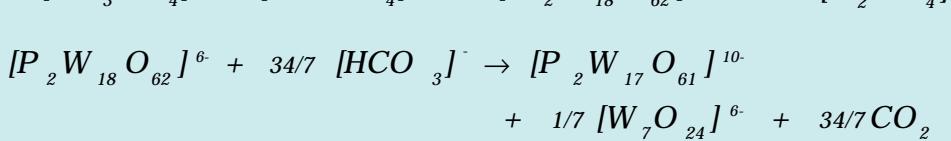
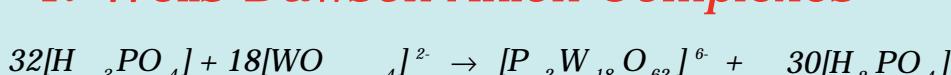
Colors of complexes:

Ce^{3+} light yellow Np^{3+} not formed

Ce^{4+} not formed Np^{4+} not formed

U^{4+} light green Am^{3+}, Cm^{3+} white

R-Wells-Dawson Anion Complexes



Reactions with R^{3+} & R^{4+}



70-90% Yields ~70%

Colors of complexes:

Ce^{3+} burgundy Np^{3+} blue*

Ce^{4+} yellow Np^{4+} yellow

U^{4+} violet Am^{3+} orange

* heteropoly blue form

R-Lindquist Anion Complexes



Reactions with high-valent R



in alkaline solutions, $R = Np$:

\rightarrow red

Same in solid and solution

$DnO H_2O$ coordinated to R

$[R^{4+}P_5W_{30}O_{110}]^{11-12-}$

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Under investigation

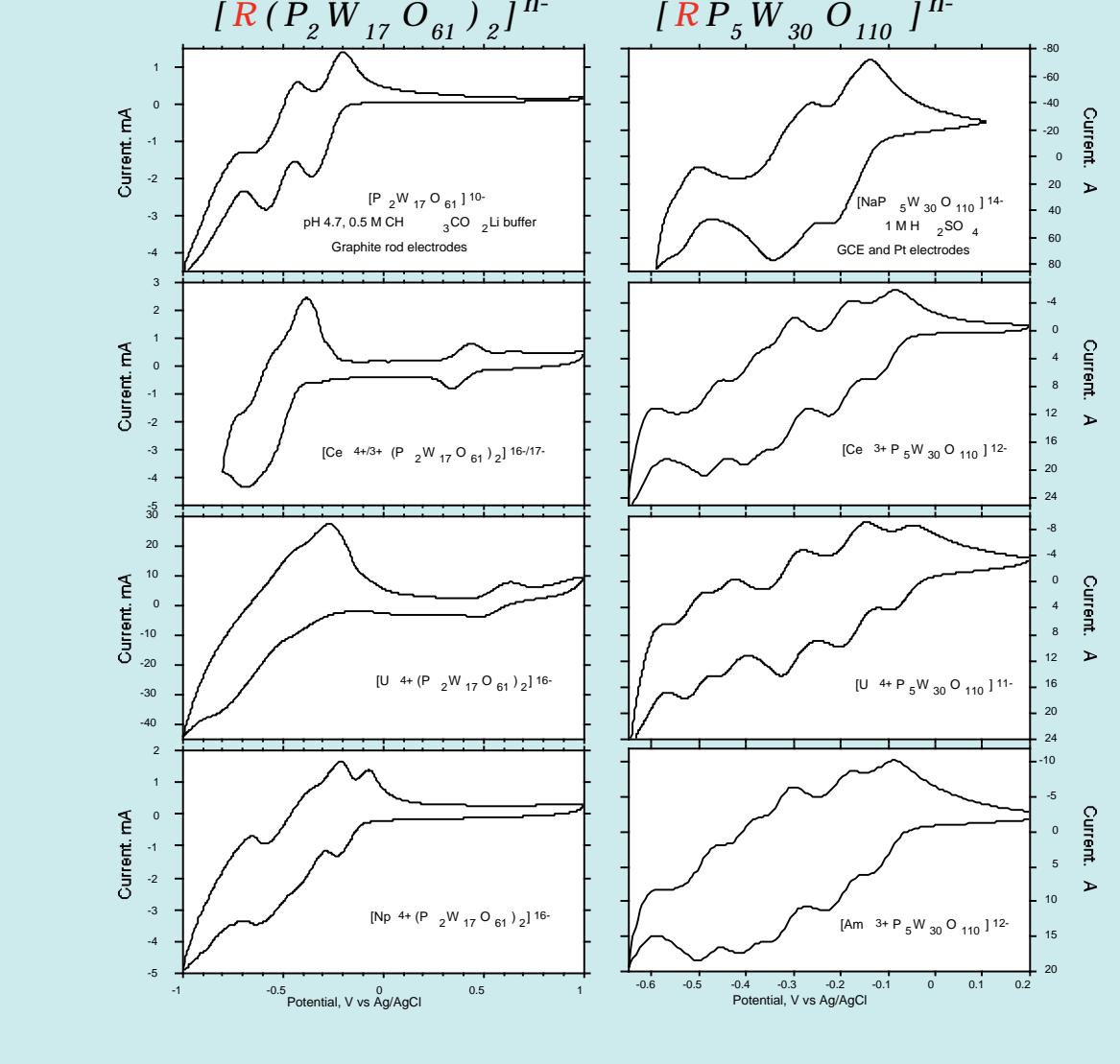
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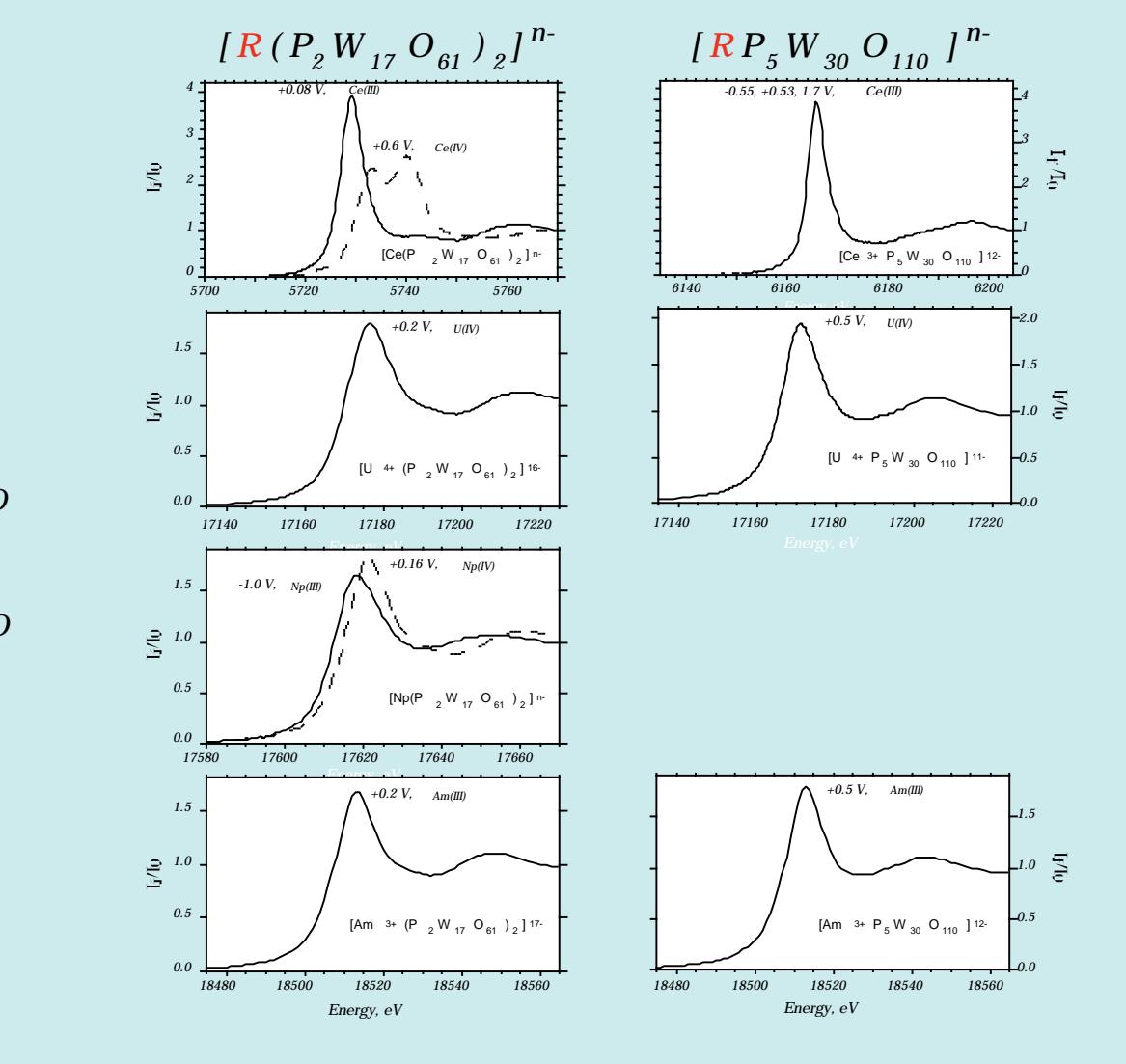
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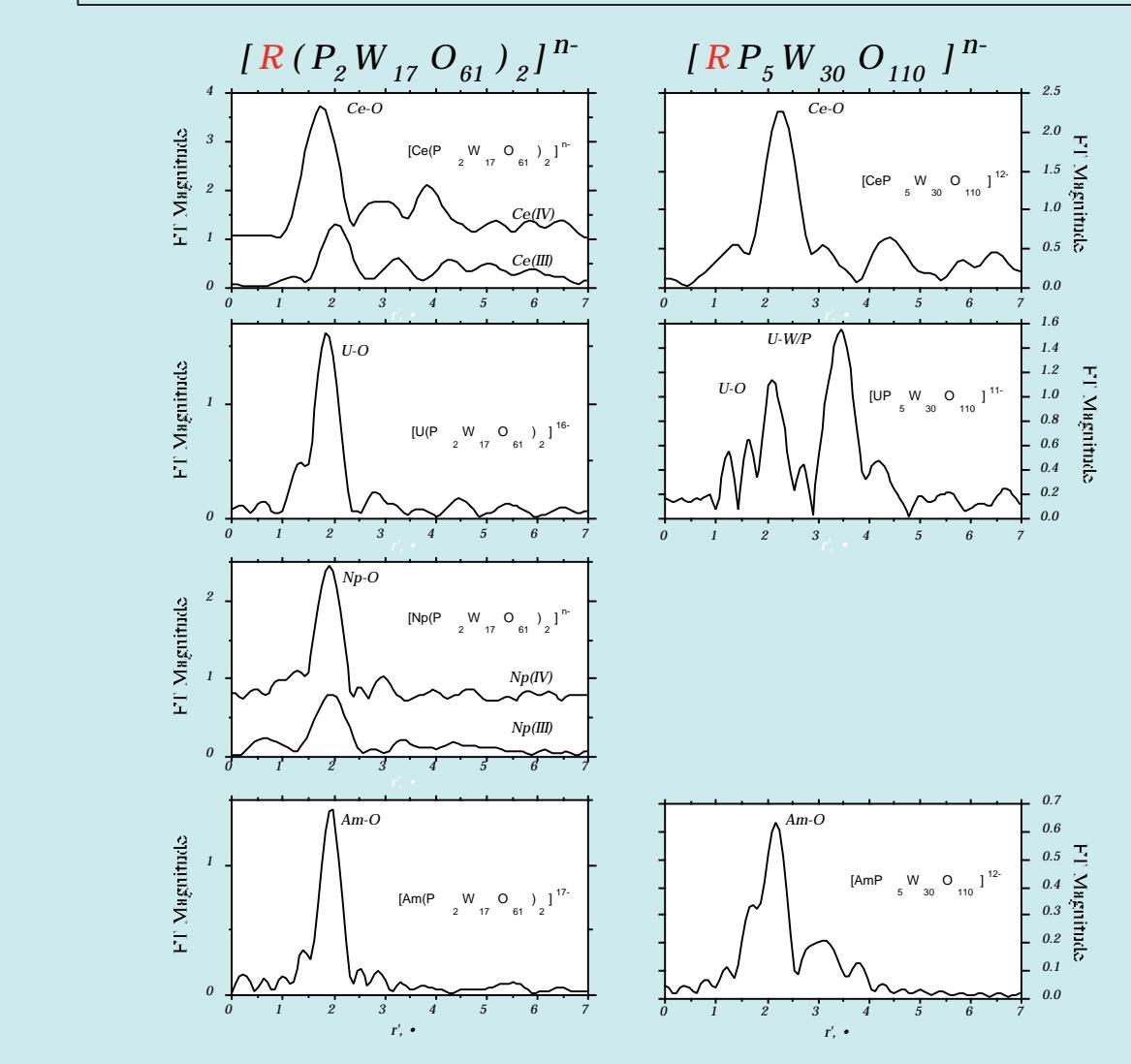
ELECTROCHEMISTRY



XANES, X-ray Absorption Near Edge Structure



EXAFS, Extended X-ray Absorption Fine Structure



OPTICAL FLUORESCENCE



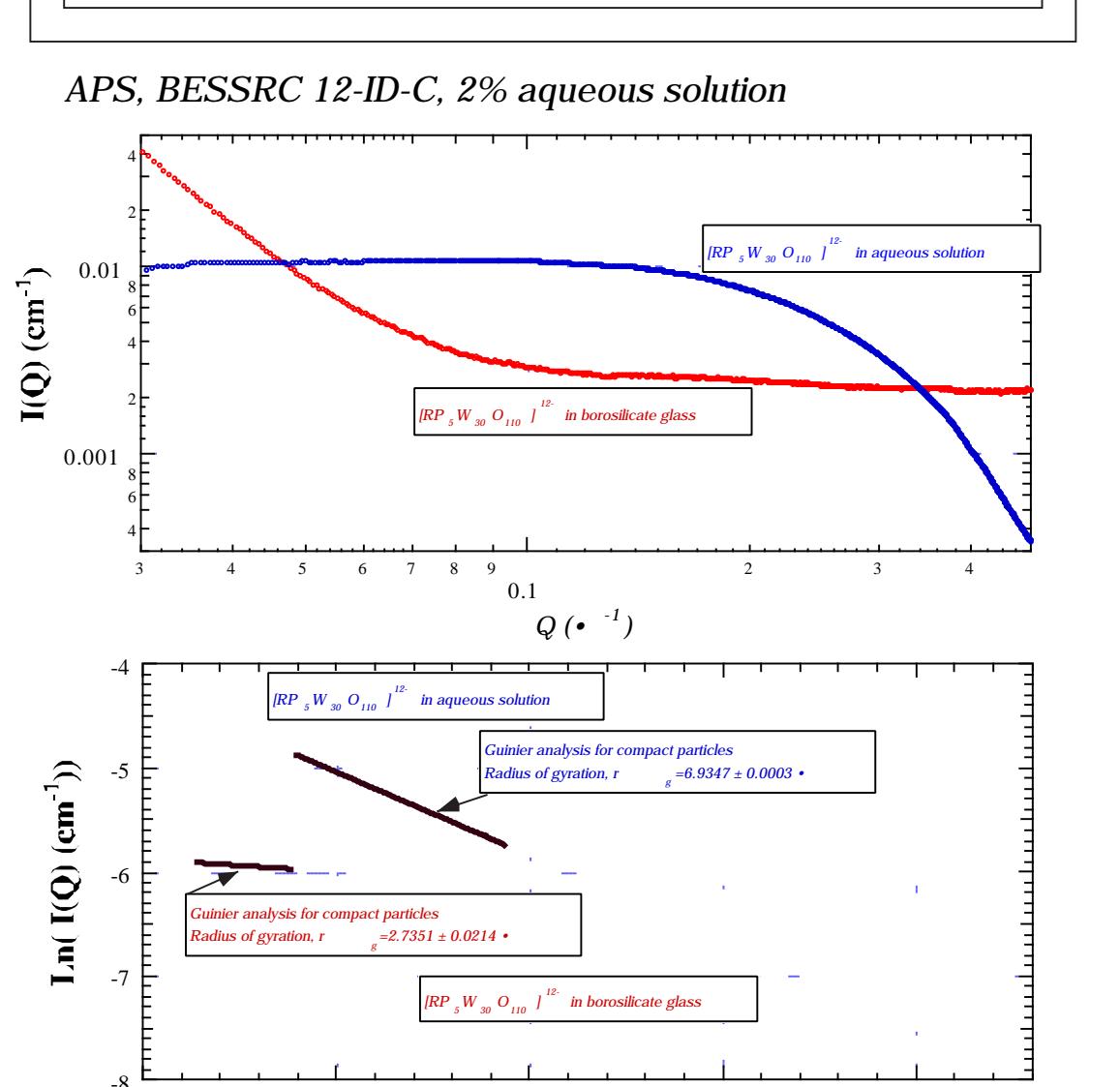
No evidence for $[Eu^{3+}P_5W_{30}O_{110}]^{12-}$. Broad peak (500 nm) suggests presence of Eu

GLASS PREPARATION

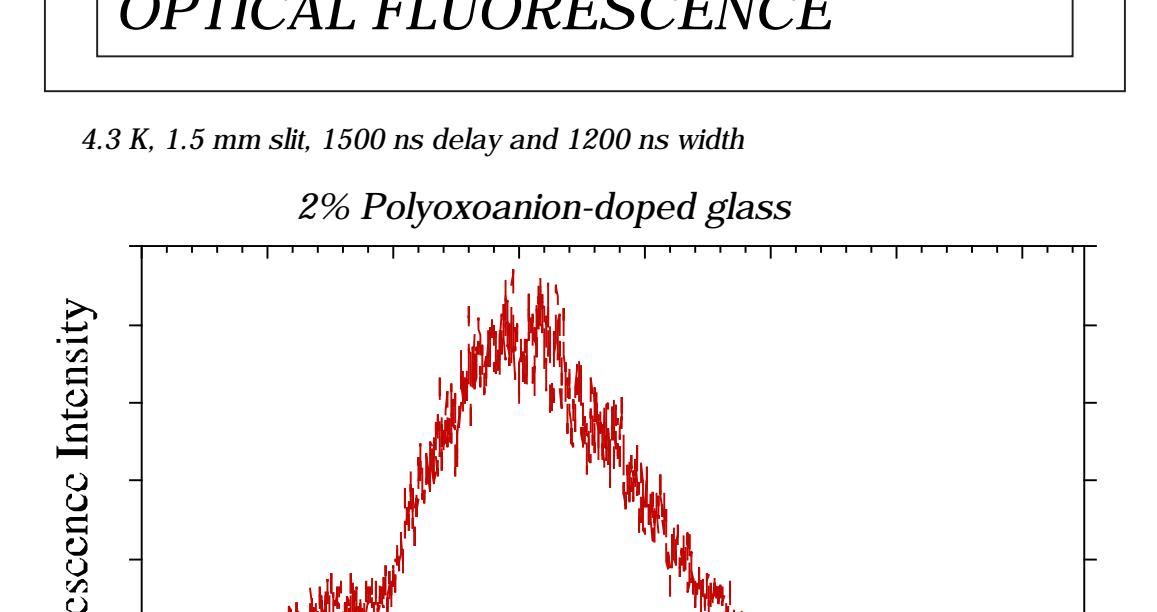
Borosilicate base glass:
 B_2O_3 (12%), SiO_2 (63.2%), Na_2O (20%), Al_2O_3 (4.8%)
Polyoxoanion-doped borosilicate glass:
1B5% $[R^{3+}P_5W_{30}O_{110}]^{12-}$ in Pt crucible:
50 °C/min to 800 °C, 4 hr in air
100 °C/min to 1500 °C, 5 hr in air
furnace cool to RT in air.
No crystalline phases observed by XRD, Cu K α radiation

DID CLUSTER DISSOLVE IN GLASS?

Small-Angle X-ray Scattering



OPTICAL FLUORESCENCE



No evidence for $[Eu^{3+}P_5W_{30}O_{110}]^{12-}$. Broad peak (500 nm) suggests presence of Eu

XAFS, X-ray Absorption Fine Structure

