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Actinide Chemistry in Chloride Solutions

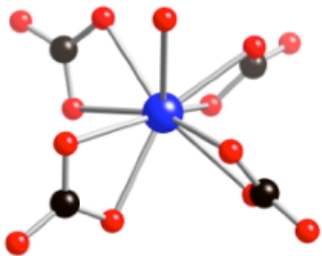
Wolfgang Runde
SPO-SC, runde@lanl.gov

Overview

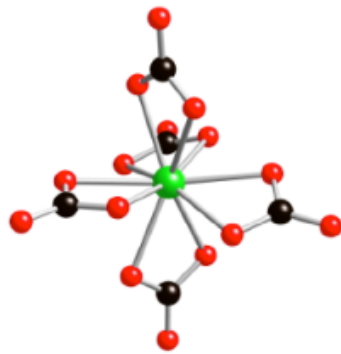
- Background
- An(V,VI) Interactions with Chloride
 - Solid State
 - Solution
- Impact on An(V,VI) Solubility
- Formation of Ternary Species
- Conclusion

Historical Approach: Binary Complexes

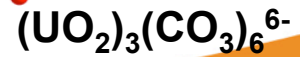
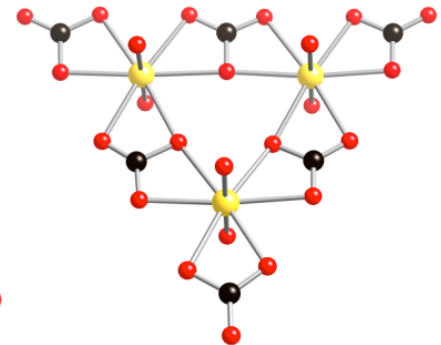
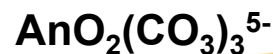
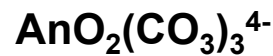
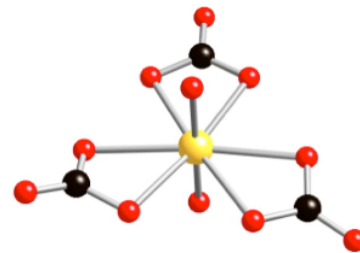
- Historically, actinide chemistry focused on acidic conditions associated with processing and separation of uranium and plutonium.
- With changes in waste management approaches, near-neutral conditions of environmental settings initiated decades of speciation studies on light actinides (Th-Cm) in their oxidation states III-VI.
- High ionic strength environments became of interest with the exploration of geologic salt formations as nuclear waste repositories.
- Thermodynamic data determined for many (binary) actinide species and evaluated by NEA.
- Limiting coordination complexes structurally assessed for oxidation states III-VI.



Runde et al. *I.C.* (2000), 39, 1050.

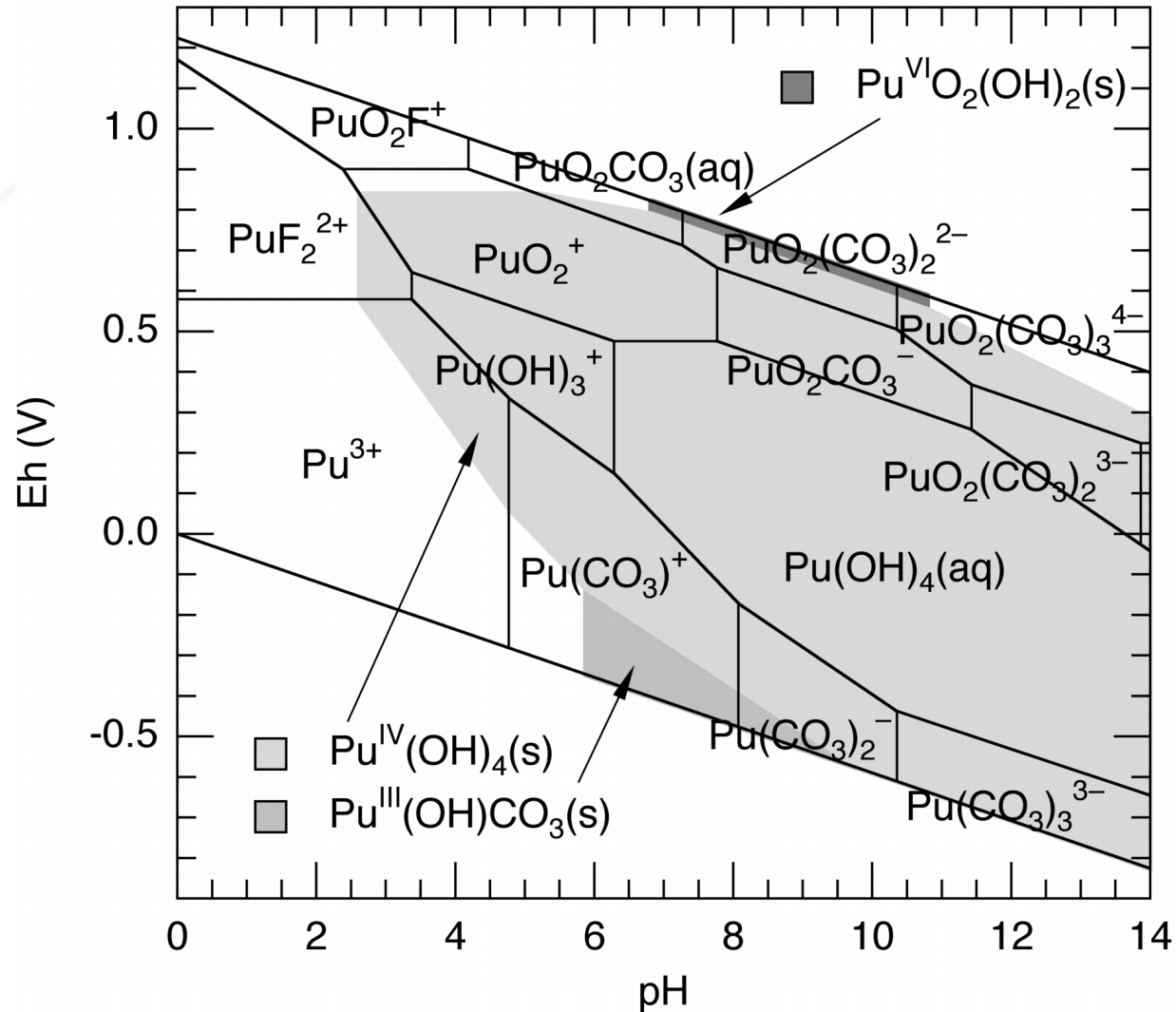


Clark et al. *I.C.* (1998), 37, 2893.



Allen et al. *I.C.* (1995), 34, 4797.

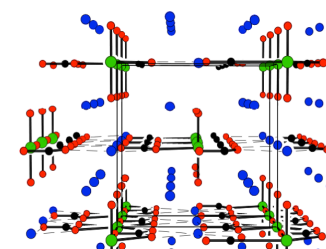
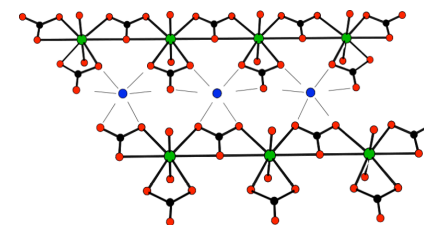
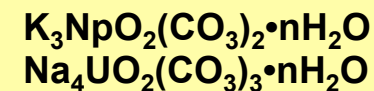
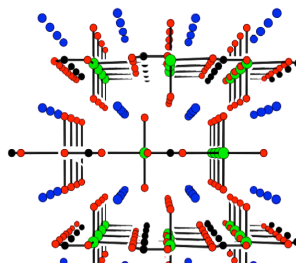
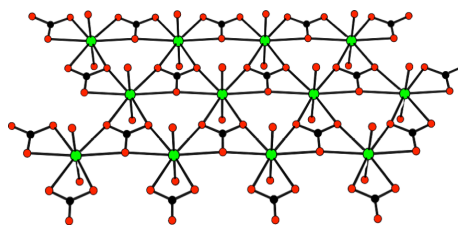
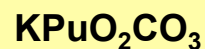
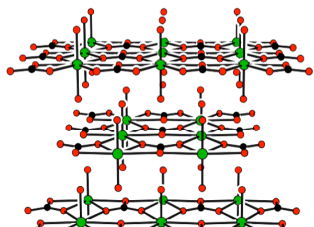
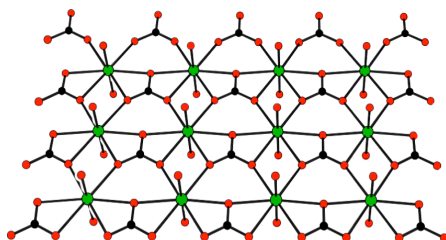
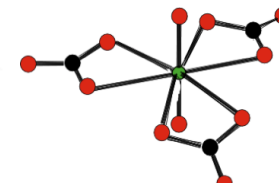
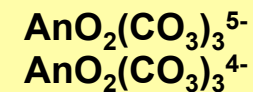
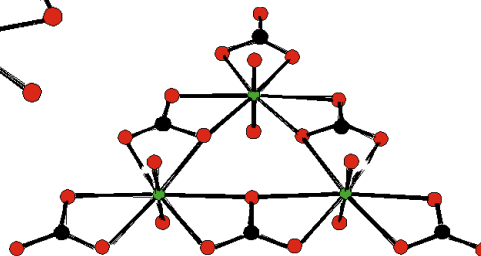
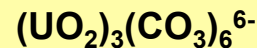
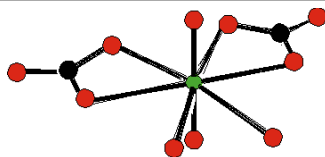
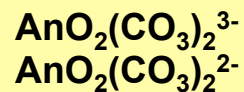
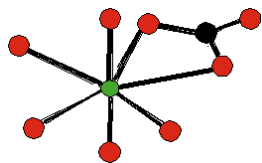
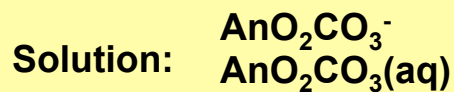
Plutonium Oxidation State Stabilities



Reilly, Runde, and Neu, *Geochim. Cosmochim. Acta* **2007**, 71, 2672-2679.

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Actinide(V,VI) Carbonate Structures



Storage and Disposal of Radioactive Waste

Interim Storage Facilities (Hanford, INEEL etc.):

- About 100 million gallons of liquid radioactive wastes (1.2 million gallons acidic liquid waste).
- Complex mixture of hydroxide, nitrate, phosphate, silicate etc. salts.
- Pretreatment essential for HLW volume reduction and vitrification.



Nuclear Waste Repositories:

- Licensed disposal in geologic salt formation.
- Site-specific brines contain complex mixture of Na^+ , K^+ , Mg^{2+} , and Cl^- , SO_4^{2-} , OH^- , CO_3^{2-} .
- Chloride is known to stabilize higher (more soluble) oxidation states of Pu.
- Actinide speciation in chloride media is critical for risk assessment.

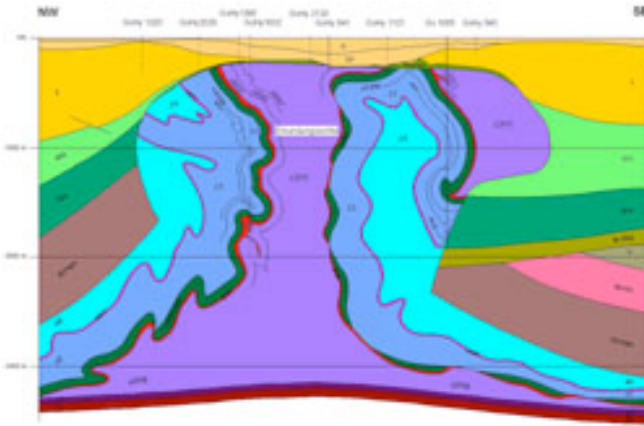
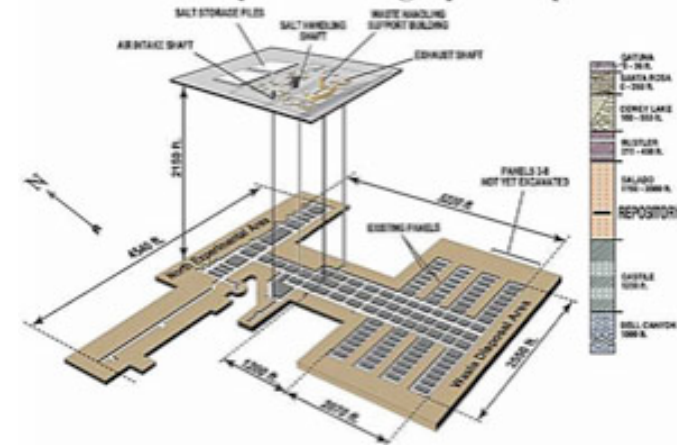
Geologic Salt Repositories



Waste Isolation Pilot Plant in New Mexico, USA

- Approved disposal site for mixed TRU waste operated since 1999.
- Over 80,000 cubic meters wastes emplaced at WIPP
- Site-specific brines contain complex mixture of Na^+ , K^+ , Mg^{2+} , and Cl^- , SO_4^{2-} , OH^- , CO_3^{2-} .

WIPP Facility and Stratigraphic Sequence



Gorleben, Asse in Germany

- About 126,000 barrels (LL, IM) are located in the Asse salt mine
- Disposal in salt dome at Gorleben abandoned.
- Actinide speciation in chloride media is critical for risk assessment.

Geologic Salt Repositories



	Salado Brine A		Castile	
Major Constituents	Concentration (mol/L)	[Cl ⁻] (mol/L)	Concentration (mol/L)	[Cl ⁻] (mol/L)
Major Constituents				
MgCl ₂ •6H ₂ O	1.44	2.87	0.02	0.04
NaCl	1.71	1.71	4.48	4.48
KCl	0.77	0.77	0.10	0.10
Na ₂ SO ₄	0.04	0.00	0.17	0.00
Na ₂ B ₄ O ₇ •10H ₂ O	0.01	0.00	0.02	0.00
CaCl ₂	0.01	0.03	0.01	0.02
NaHCO ₃	0.01	0.00	0.00	0.00
NaBr	0.01	0.00	0.01	0.00
Minor Constituents	Concentration (mg/L)			
LiCl	125	0.00	0.00	0.00
RbCl	27.25	0.00	0.00	0.00
SrCl ₂ •6H ₂ O	15.00	0.00	0.00	0.00
KI	13.00	0.00	0.00	0.00
FeCl ₃ •6H ₂ O	12.50	0.00	0.00	0.00
CsCl	1.25	0.00	0.00	0.00
		5.39		4.64

Site-specific brines contain complex mixture of Na⁺, K⁺, Mg²⁺, and Cl⁻, SO₄²⁻, OH⁻, CO₃²⁻

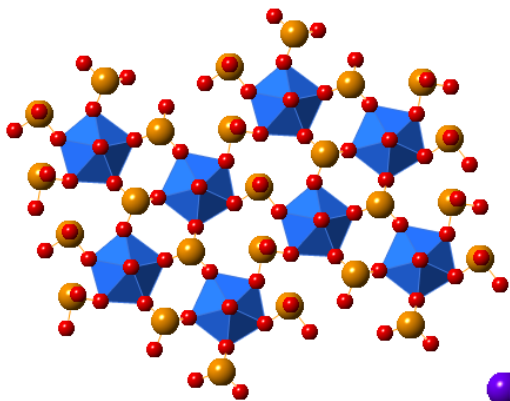


Coordination Chemistry of $[\text{AnO}_2\text{X}_4]^{2-}$

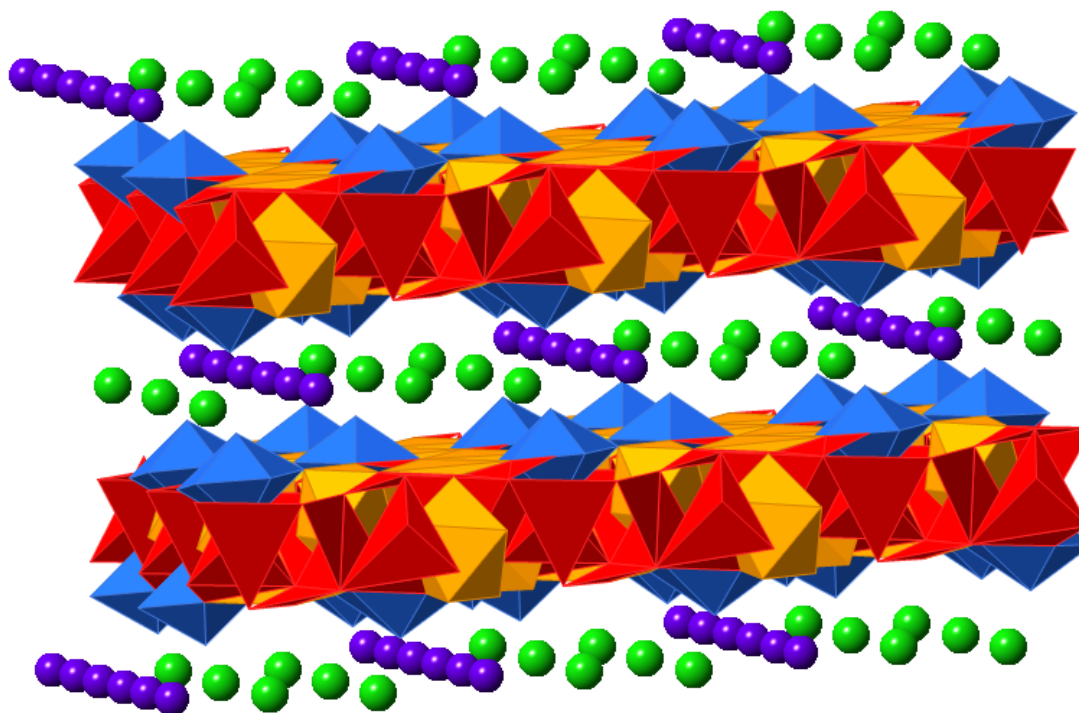
An = U, Np, Pu

X = Cl, Br

Solid State Compounds: Intercalation of Chloride



Examples:

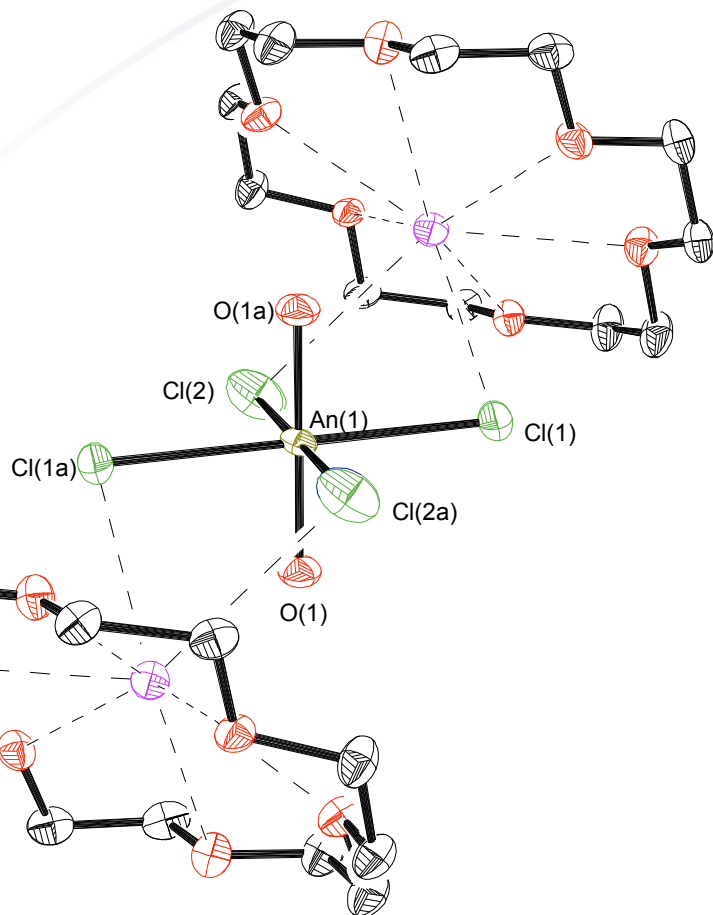


Bean et al., *J. Solid State Chem.* **2004**, 177, 1346-1351.

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[K(18-crown-6)]₂[UO₂X₄] X= Cl, Br

Sandwich-type compound with same coordination geometry for X = Cl and Br

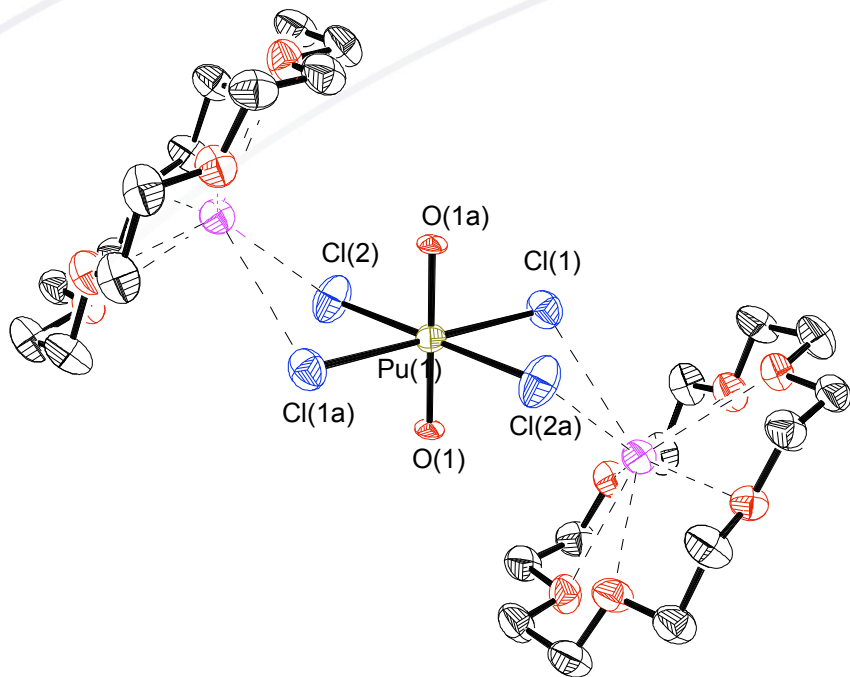


UO₂Cl₄²⁻: Monoclinic, $P2_1/c$
 $a=10.1307(5)$ Å, $b=10.0450(5)$ Å, $c=19.4990(9)$ Å
U=O 1.7723(16) Å
U-Cl(1) 2.6847(7) Å
U-Cl(2) 2.6771(7) Å
K-Cl(1) 3.3451(9) Å
K-Cl(2) 3.2974(9) Å

UO₂Br₄²⁻: Monoclinic, $P2_1/c$
 $a=10.2472(5)$ Å, $b=10.0343(5)$ Å, $c=19.7082(9)$ Å
U=O 1.769(2) Å
U-Br(1) 2.8230(4) Å
U-Br(2) 2.8188(4) Å
K-Br(1) 3.3744(9) Å
K-Br(2) 3.4852(10) Å

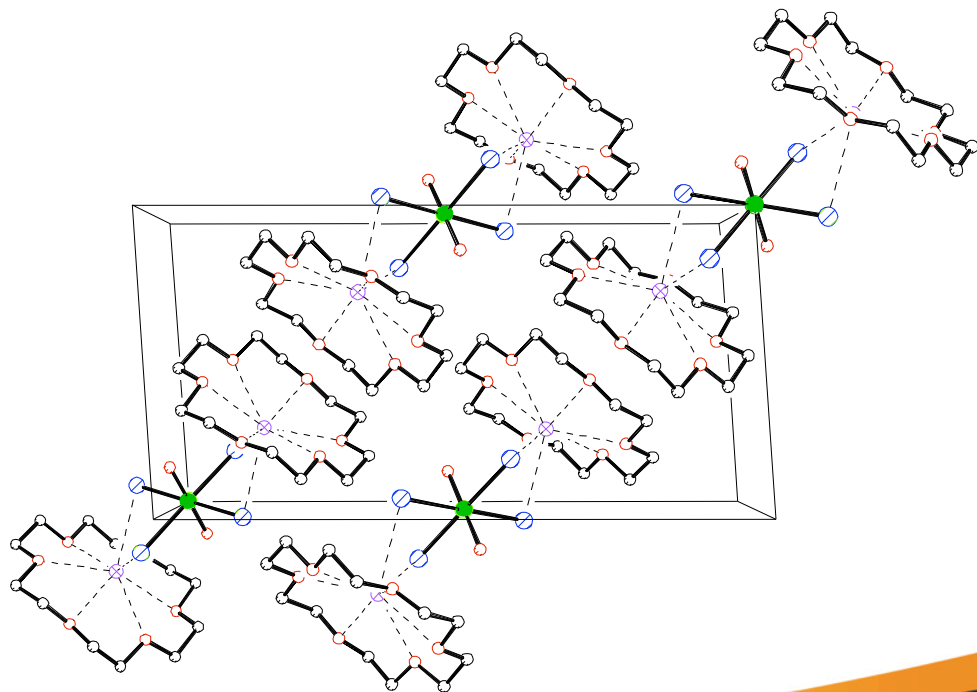
Danis et al., *Inorg. Chem.* **2001**, *40*, 3389-3394.

[K(18-crown-6)]₂[AnO₂Cl₄] where An = U, Np, Pu



	An=O	An-Cl	K-Cl
U	1.772(1)	2.68(1)	3.32(2) Å
Np	1.785(7)	2.66(1)	3.30(1) Å
Pu	1.737(4)	2.66(1)	3.29(1) Å

Pu=O	1.737(4) Å
Pu-Cl	2.657(2) Å
K-Cl(1)	3.278(2) Å
K-Cl (2)	3.287(2) Å

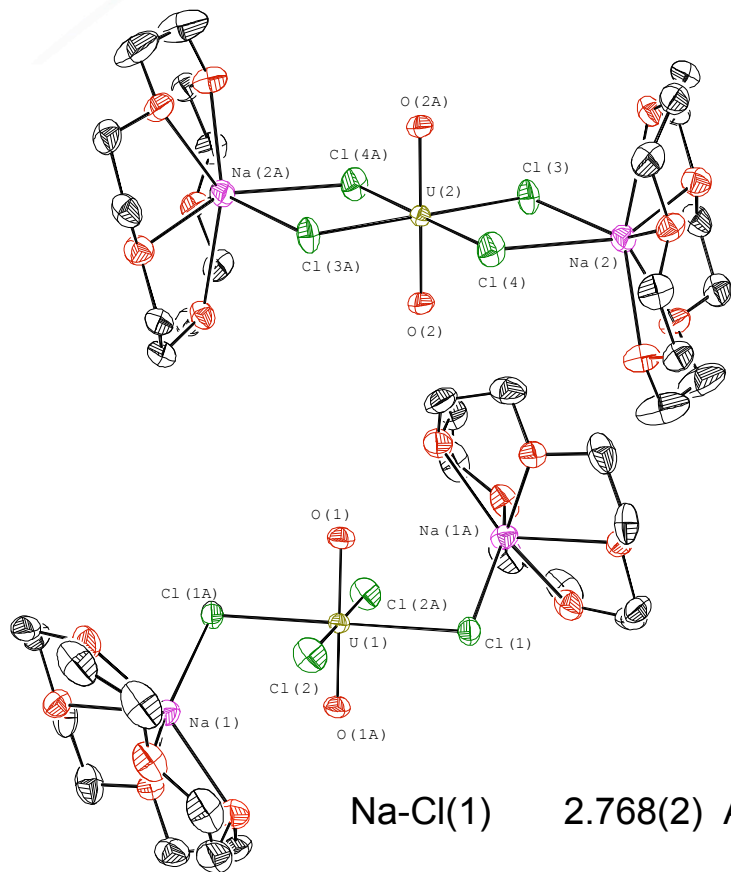


An(VI) Halides: (15-crown-5)₂[UO₂X₄] X= Cl, Br

[Na(15-crown-5)]₂[UO₂Cl₄]

Two coordination modes within unit cell

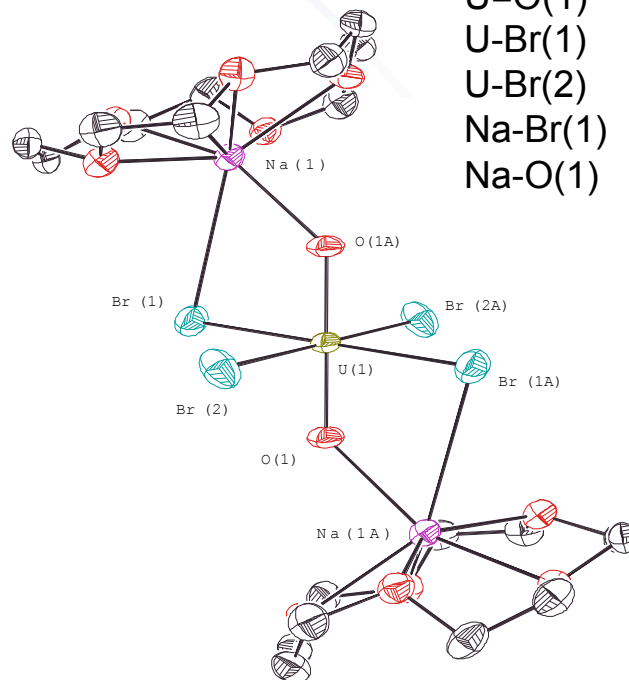
U-O(1)	1.764(2) Å
Na-Cl(1)	3.024(3) Å



[Na(15-crown-5)]₂[UO₂Br₄]

Coordination geometry changes with X

U=O(1)	1.780(3) Å
U-Br(1)	2.8191(4) Å
U-Br(2)	2.8091(4) Å
Na-Br(1)	3.305(2) Å
Na-O(1)	2.456(3) Å



Int. Tables for X-Ray Cryst.:

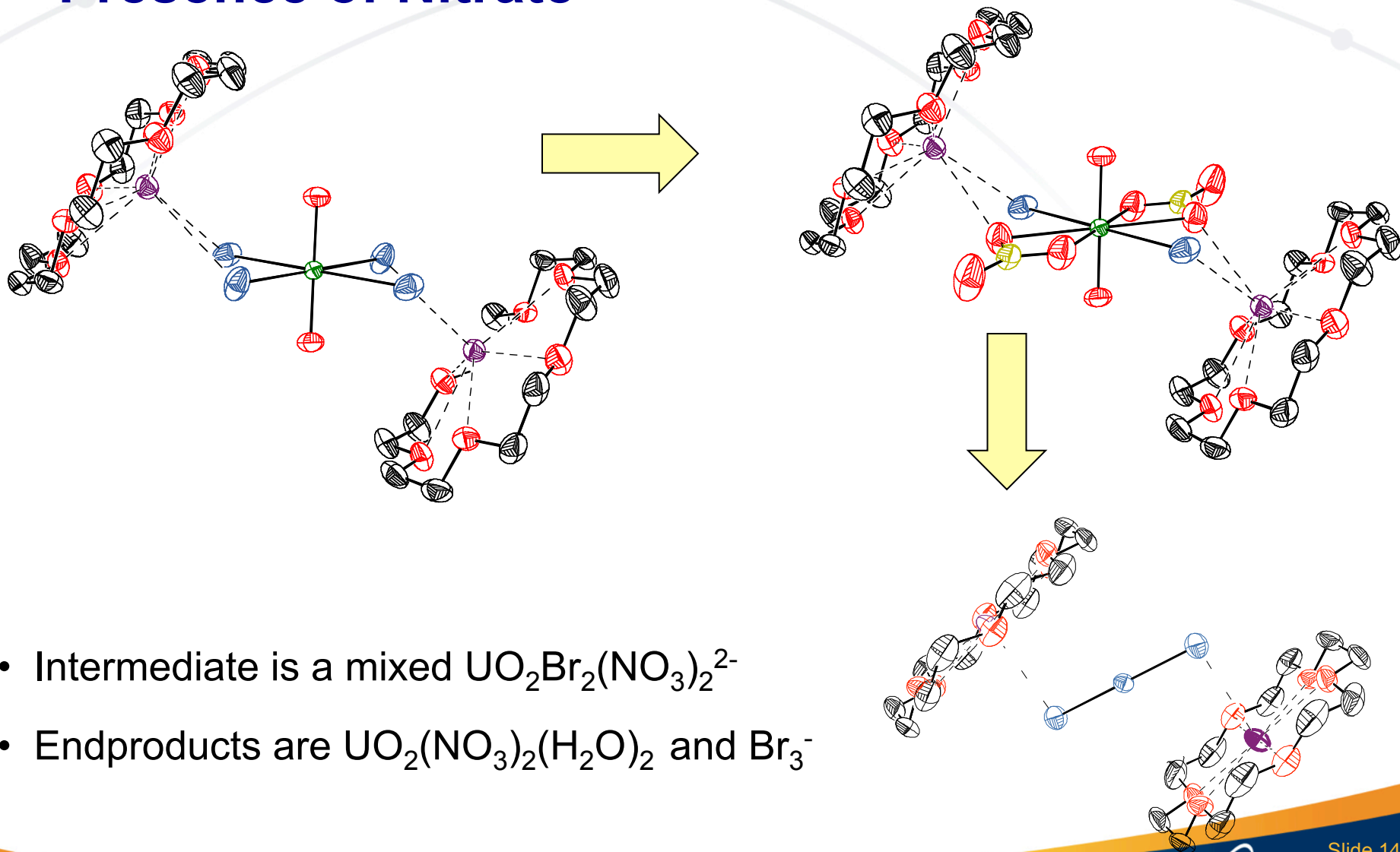
NaCl	2.8199(7) Å
NaBr	2.983(3) Å

Danis et al., *Inorg. Chem.* **2001**, *40*, 3389-3394.

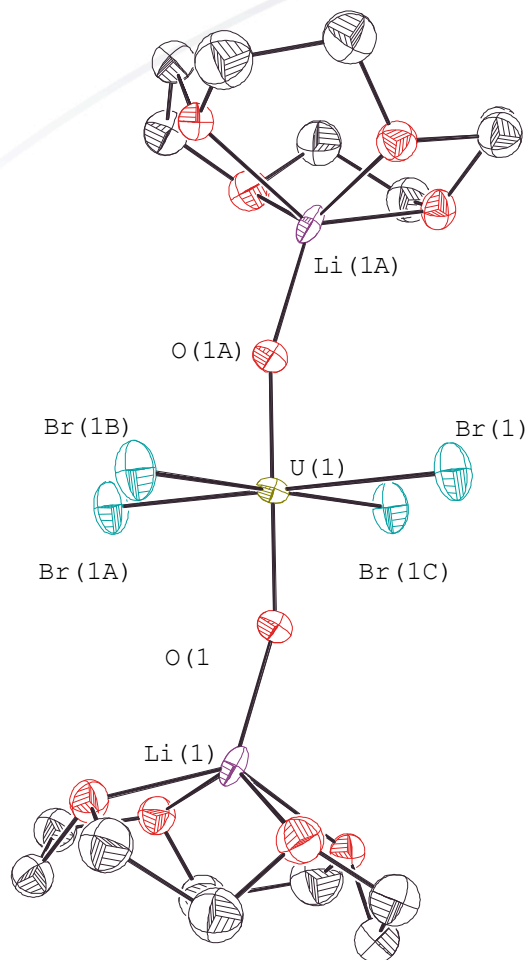
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Stability of $[K(18\text{-crown-6})]_2[UO_2Br_4]$ in the Presence of Nitrate



[Li(12-crown-4)]₂[UO₂X₄] X= Cl, Br



Same coordination geometry for X = Cl and Br

Orthorhombic, *Fmm2*

$a=13.340(1)$ Å, $b=14.963(1)$ Å, $c=13.151(1)$ Å

U=O 1.767(9) Å

U-Cl(1) 2.61(7) Å

U-Cl(2) 2.65(7) Å

Li-O(1) 1.89(2) Å

Monoclinic, *Cmca*

$a=13.656(1)$ Å, $b=15.039(1)$ Å, $c=13.409(1)$ Å

U=O 1.79(1) Å

U-Br(1) 2.793(1) Å

Li-O(1) 1.89(3) Å

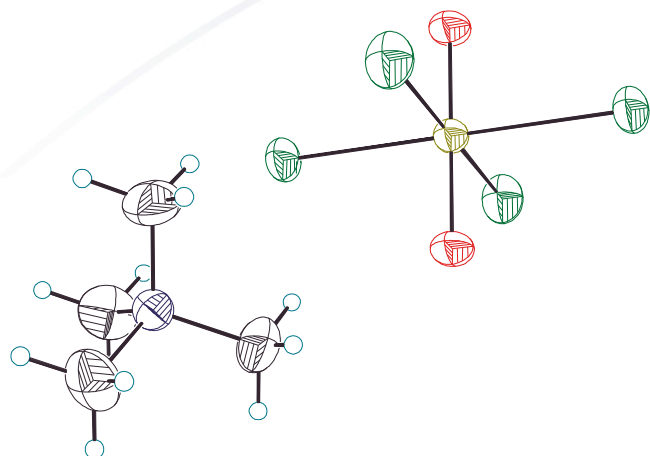
Danis et al., *Inorg. Chem.* **2001**, *40*, 3389-3394.

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[TMA(18-crown-6)]₂[UO₂Cl₄] and [H₃O(18-crown-6)]₂[UO₂Br₄]

Discrete UO₂Cl₄²⁻ Anions within the Lattice



[TMA(18-crown-6)]₂[UO₂Cl₄]

Tetragonal, $P4_2/mnm$

$a=9.1634(5)$ Å, $b=9.1634(5)$ Å, $c=11.5259(8)$ Å

U=O 1.770(4) Å

U-Cl(1) 2.6484(19) Å

U-Cl(2) 2.6781(15) Å

[H₃O(18-crown-6)]₂[UO₂Br₄]

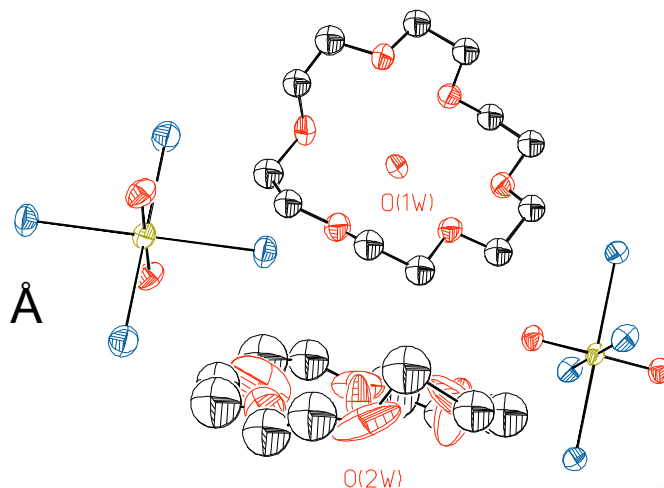
Monoclinic, $P2_1/c$

$a=20.1163(11)$ Å, $b=19.2224(9)$ Å, $c=10.2153(5)$ Å

U=O 1.765(5) Å

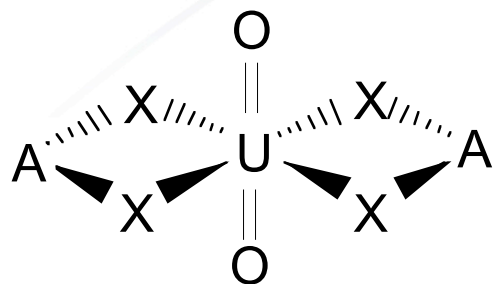
U-Cl(1) 2.8339(8) Å

U-Cl(2) 2.8402(8) Å

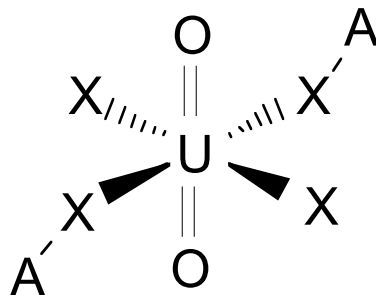


Effect of Cation on Interaction Modes

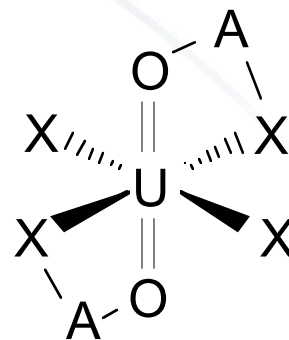
Structure Types:



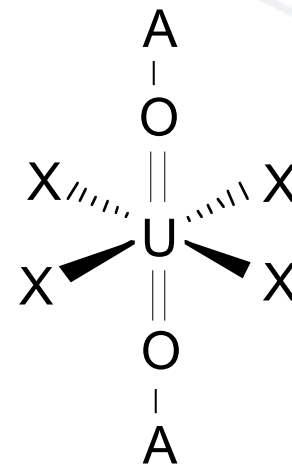
I



II



III



IV

Softer K^+ prefers this type for both Cl, Br

Hard Li prefers this Type for both Cl, Br

Na^+ adopts this type with Cl

Na^+ adopts this type with Cl, too

Na^+ adopts this type for Br

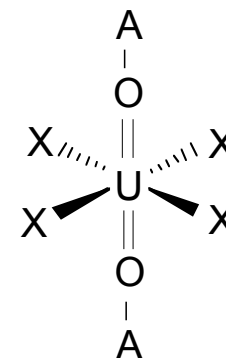
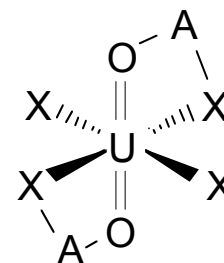
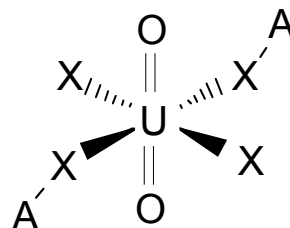
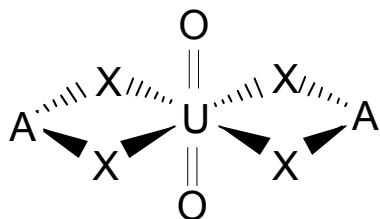
Danis et al., *Inorg. Chem.* **2001**, *40*, 3389-3394.

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Structure and Bonding in $[M(\text{crown})]_2[\text{UO}_2\text{X}_4]$

$\text{UO}_2\text{Cl}_4^{2-}$	TMA ⁺	Li ⁺	Na ⁺	K ⁺
U=O	1.770(4)	1.767(9)	1.764(2)	1.7723(16)
U-X	2.6484(19)	2.61(1)	2.693(1)	2.6847(7)
U-X	2.6781(15)	2.65(1)	2.658(1)	2.6771(7)
M-O _{Ur}		1.89(2)	-	-
M-X		-	2.768(2)	3.3451(9)



$\text{UO}_2\text{Br}_4^{2-}$	H ₃ O ⁺	Li ⁺	Na ⁺	K ⁺
U=O	1.765(5)	1.79(1)	1.780(3)	1.769(2)
U-X	2.8339(8)	2.793(1)	2.8191(4)	2.8230(4)
U-X	2.8402(8)	-	2.8091(4)	2.8188(4)
M-O _{Ur}		1.89(3)	2.456(3)	-
M-X		-	3.305(1)	3.3744(9)

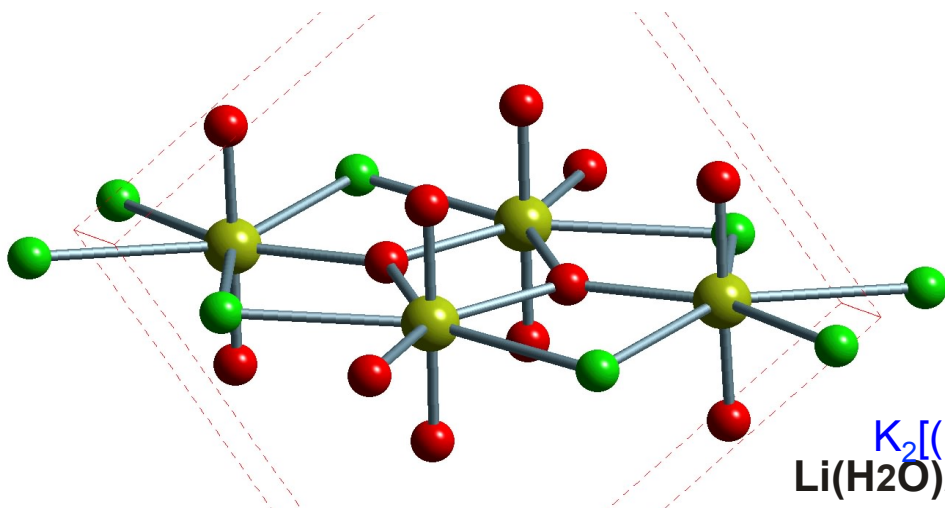
Danis et al., *Inorg. Chem.* **2001**, *40*, 3389-3394.

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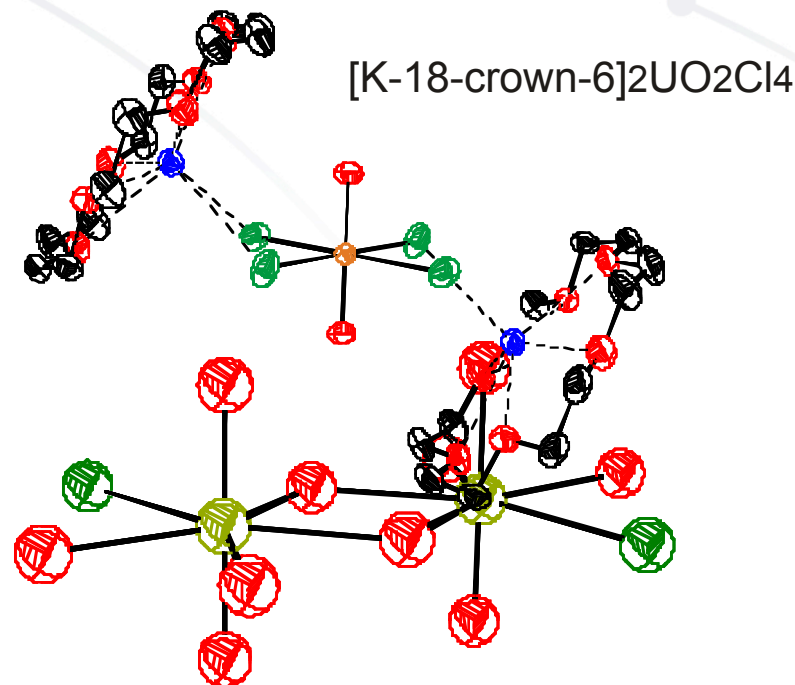
Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

Chloride Coordination in Solid States

- Intercalation
- Binary $AnO_2Cl_4^{2-}$
- Mixed-Ligand Complexes



$K_2[(UO_2)_4(\mu-O)_2(OH)_2Cl_4(H_2O)_6]$ (Perrin, 1977)
 $Li(H_2O)_2[UO_2(\mu_3-O)(\mu-Cl)_4][UO_2(\mu_3-O)_2(\mu-Cl)_2]$
 (Runde et al., 1997)



$[K-18-crown-6]_2UO_2Cl_4$

$(UO_2)_2(OH)_2Cl_2(H_2O)_4$
 Åberg, Acta Chem.
 Scand. **23** (1969), 791-810.



Actinide Interactions with Chloride:

Spectroscopic Analysis An = U, Np, Pu

Actinide Solubility and Speciation in Low NaCl

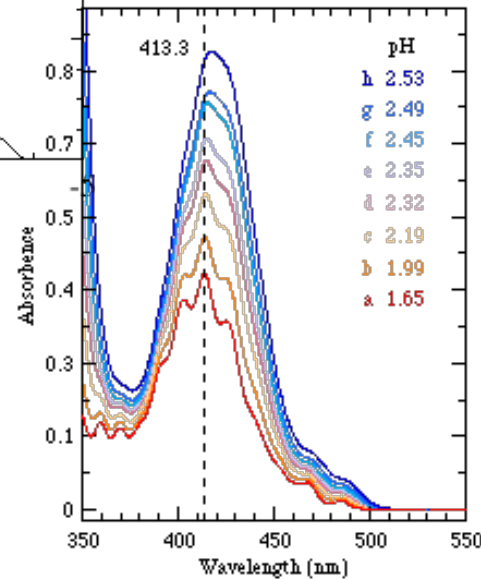
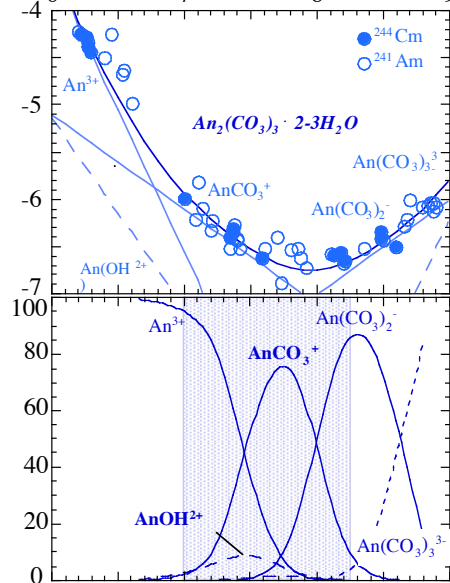
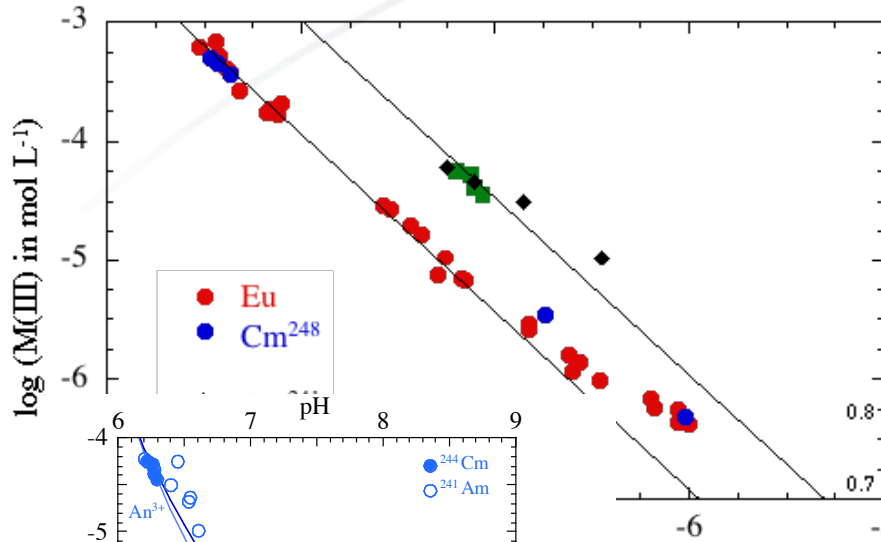


fig. 2.3.1 7.4487×10^{-2} M U(VI) in 7.4355 M of NaClO₄

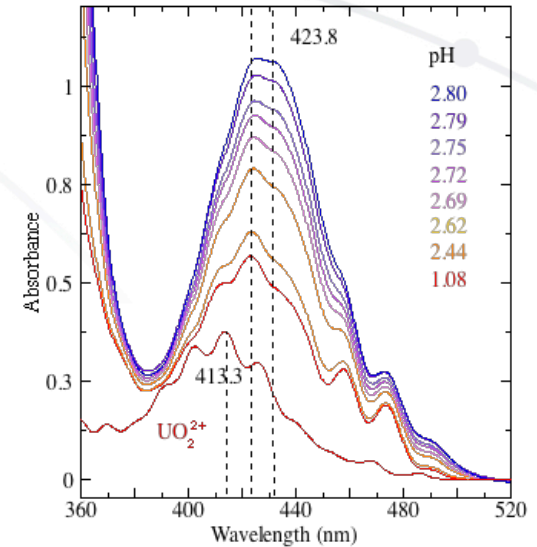
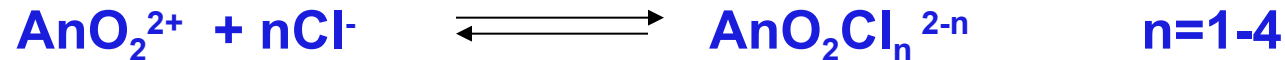


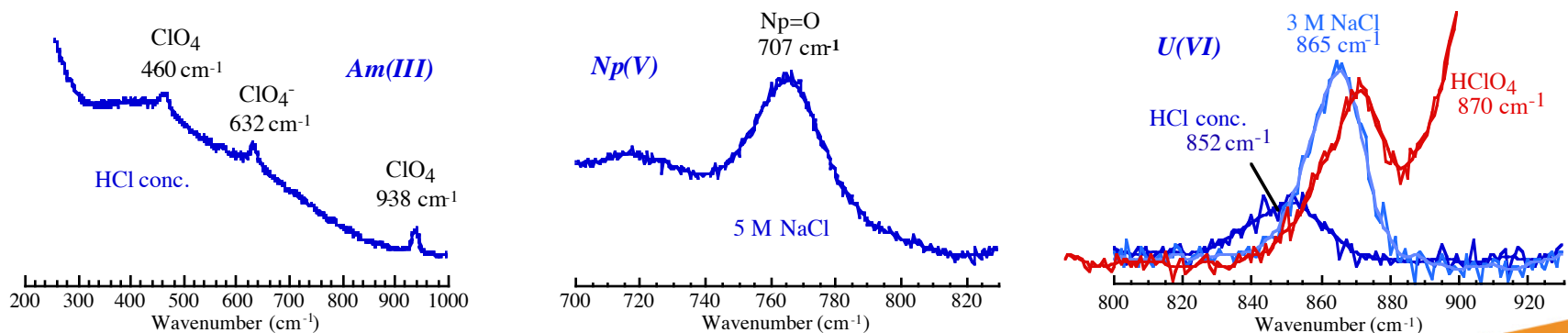
fig. 3.2.2.2 5.0469×10^{-2} M of U(VI) in 5.6618 M NaCl with increasing pH

Actinyl(VI) Interactions with Chloride

- Chloride complexes are important for disposal of TRU waste in geologic salt formation, and for Pu reprocessing and purification.
- Chloride is much weaker ligand compared to hard donor ligands such as hydroxide, carbonate, phosphate or peroxide
- EXAFS studies revealed inner-sphere complexation of An(VI), but very weak complexation of An(III, IV, V) in aqueous solutions.

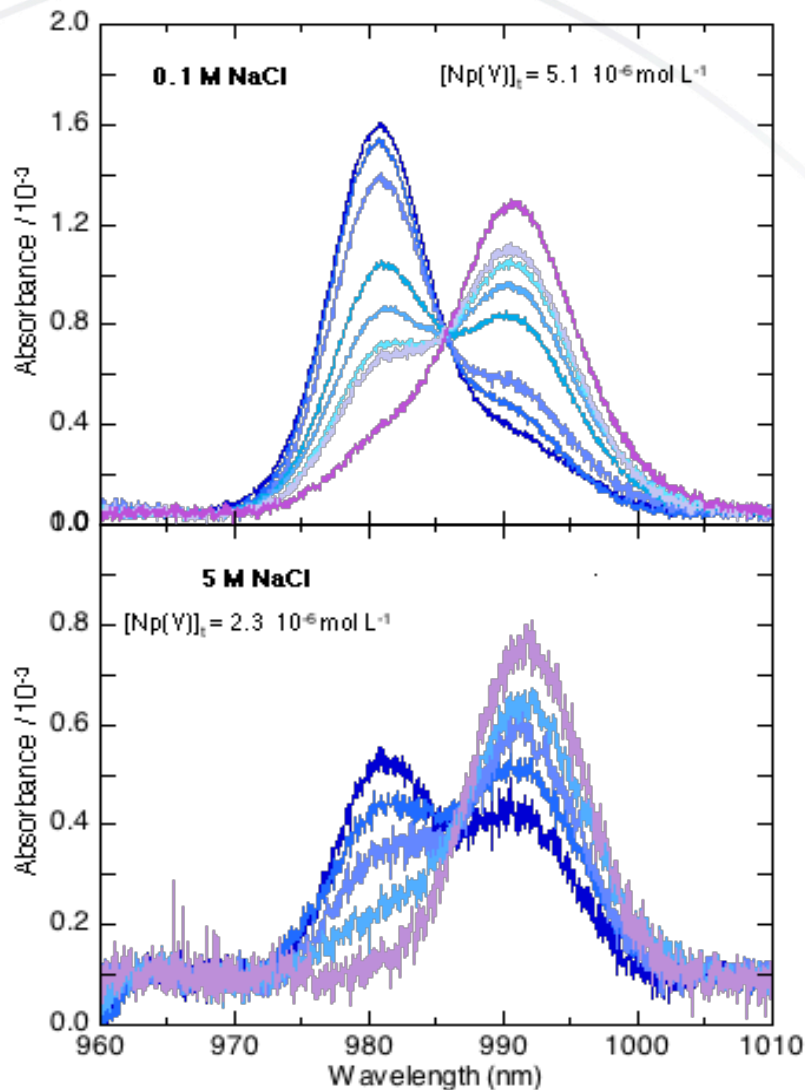
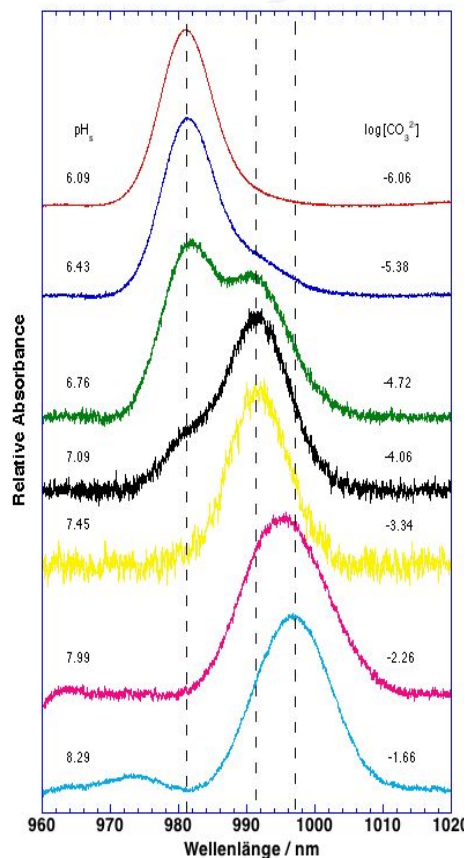


- NEA (1992) recommends stability constants for UO_2Cl^+ and UO_2Cl_2 .

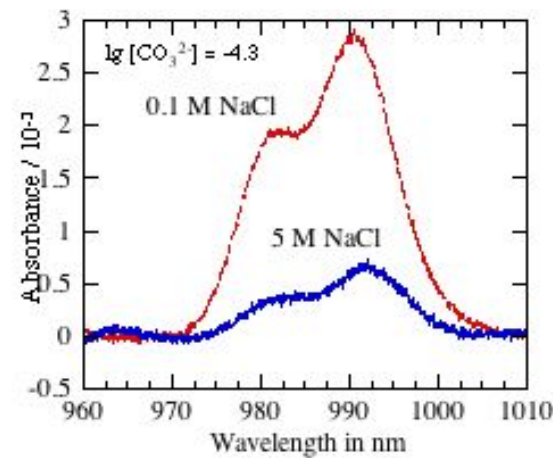


Runde et al., *Mat. Res. Soc. Symp. Proc.* 1997, 465, 693-703.
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Np(V) Carbonate Complexation in NaCl Solution

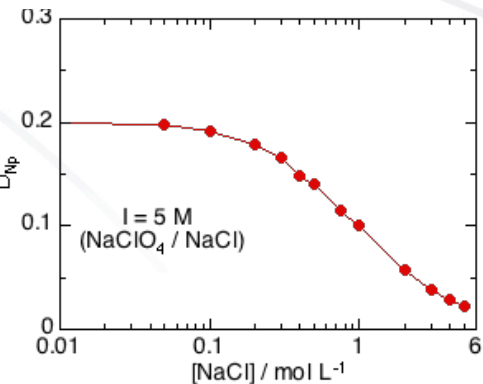
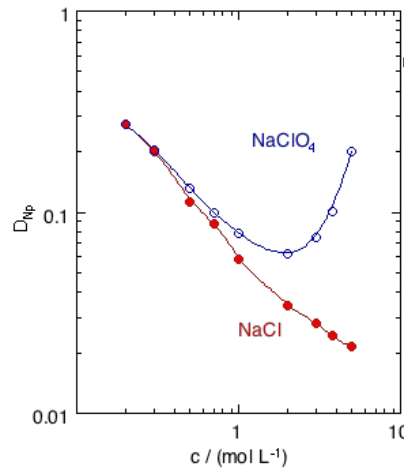
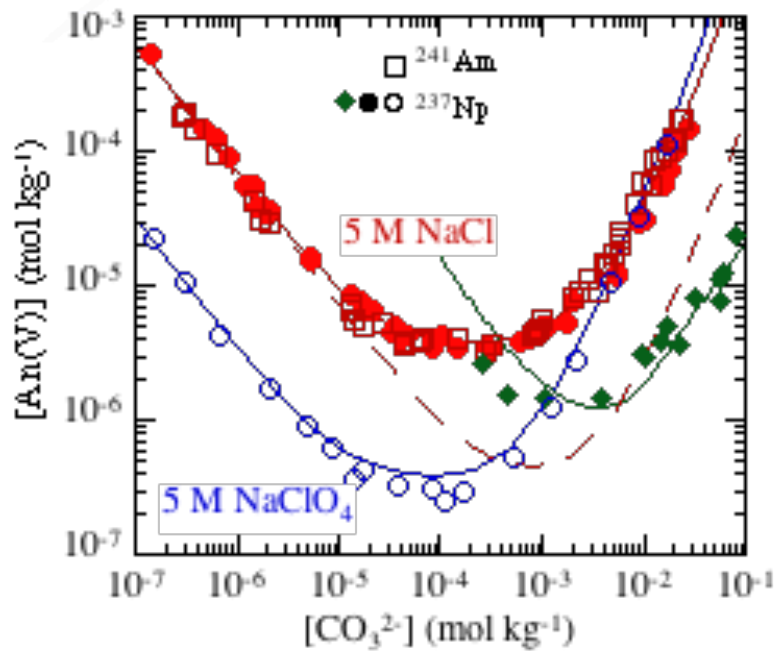


0.1 M NaCl:
980 nm for NpO_2^+
990 nm for $\text{NpO}_2\text{CO}_3^-$

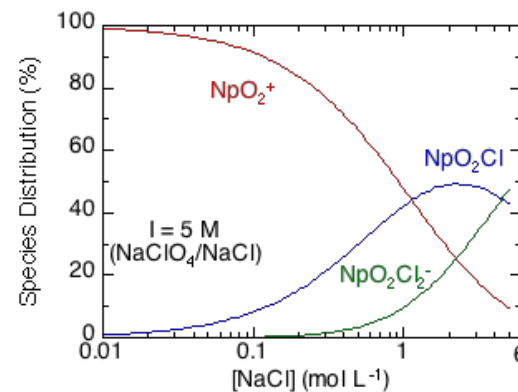


5 M NaCl:
981 nm for NpO_2^+
992 nm for $\text{NpO}_2\text{CO}_3^-$

Np(V) Interactions with Chloride



Solvent Extraction Differences in acidic NaCl/NaClO₄ solutions

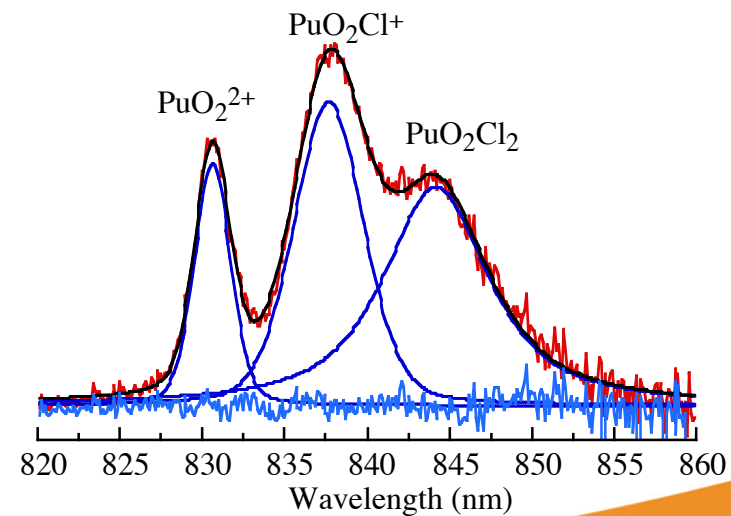
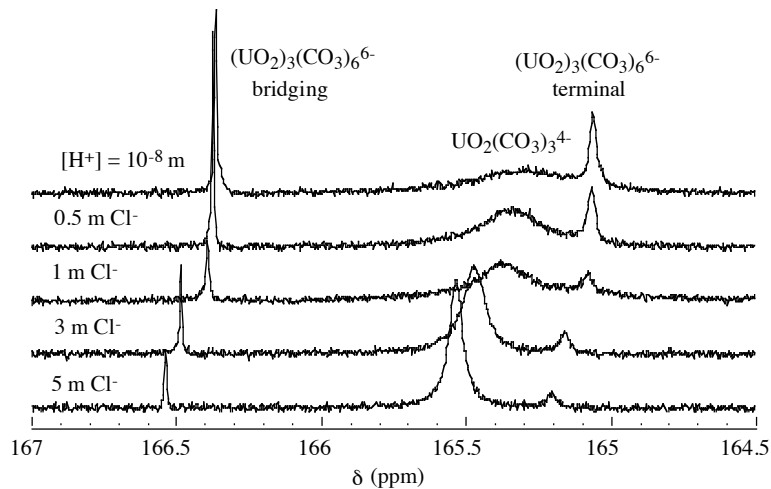
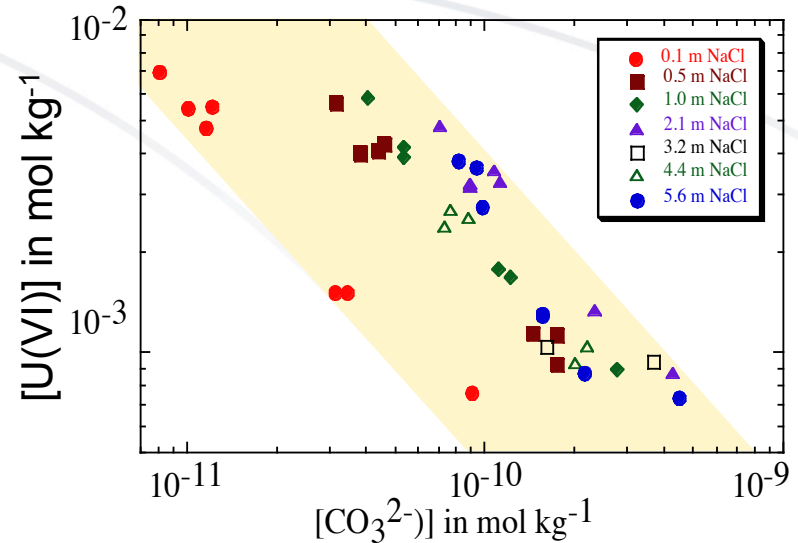


Runde et al., *Mat. Res. Soc. Symp. Proc.* **1997**, 465, 693-703.

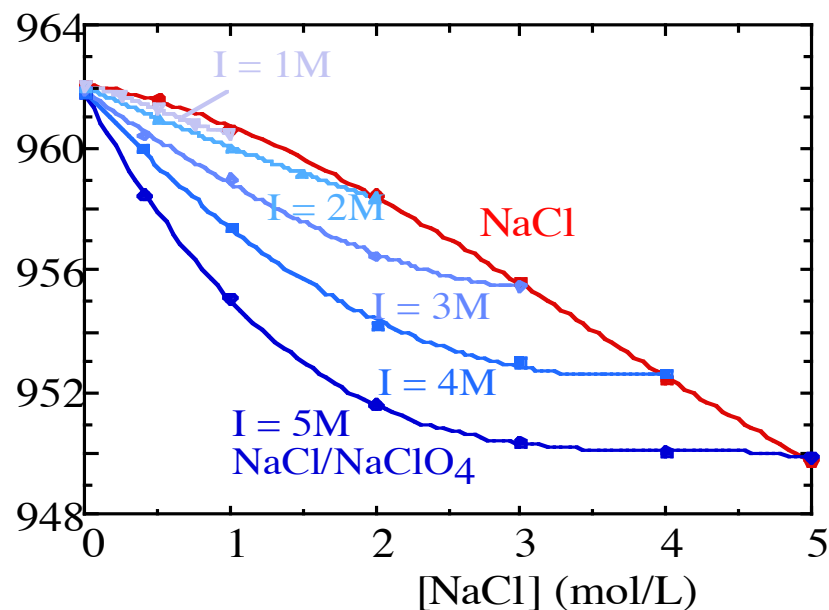
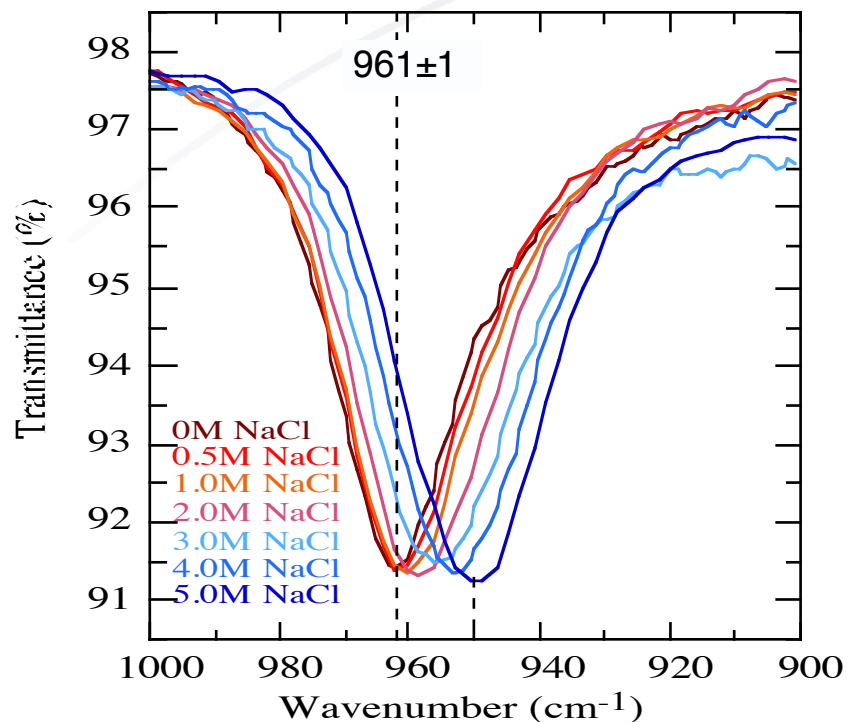
Neck and Kim, *Report KfK-5301*. **1994**.

U/Pu Halide Compl.

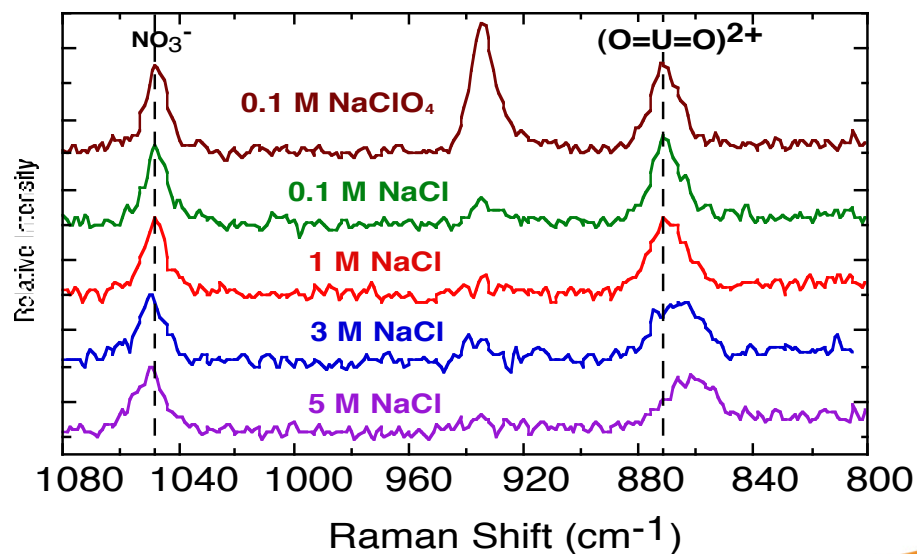
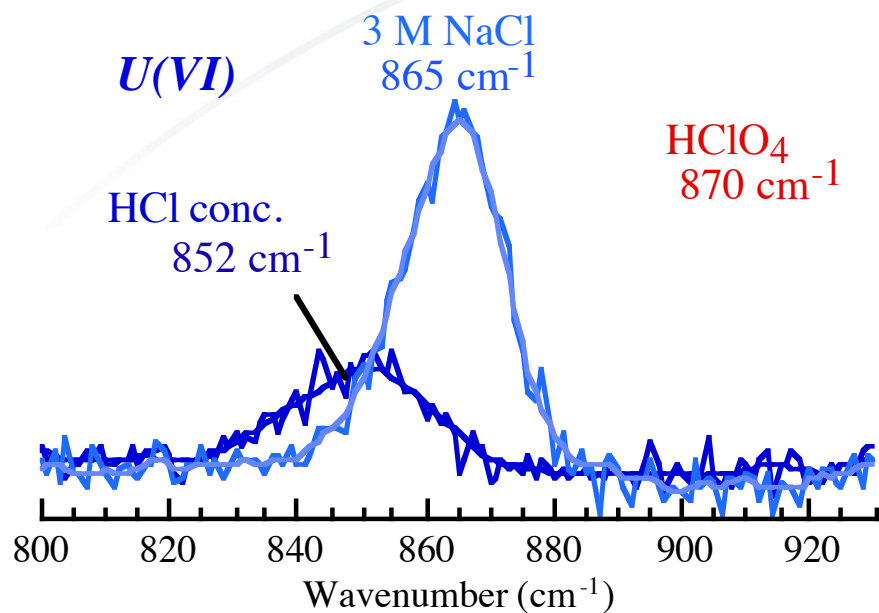
- ⇒ Increases actinyl(V) and (VI) solubility
- ⇒ Affects the stability of solution species
- ⇒ Inner-sphere vs. outer-sphere complexation
- ⇒ Separation chemistry



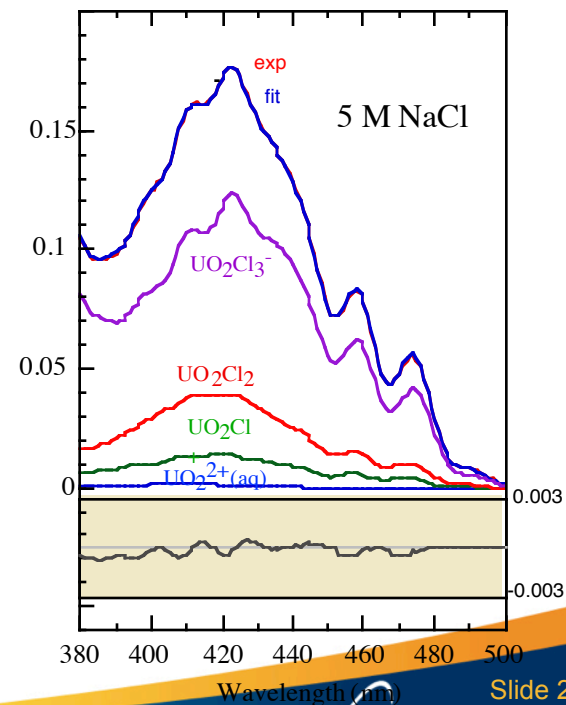
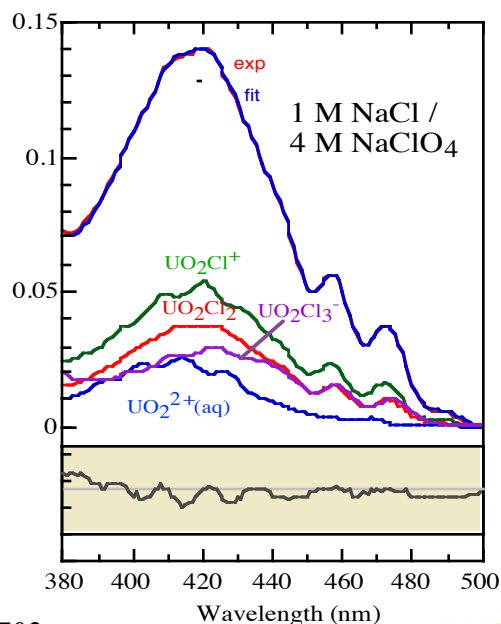
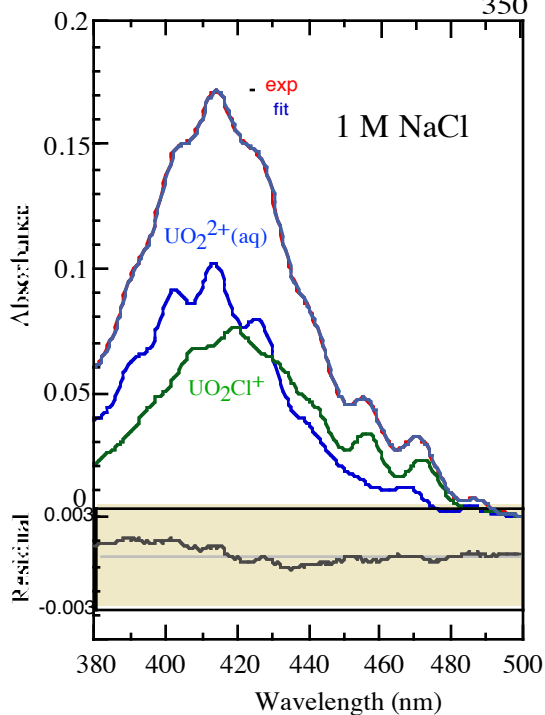
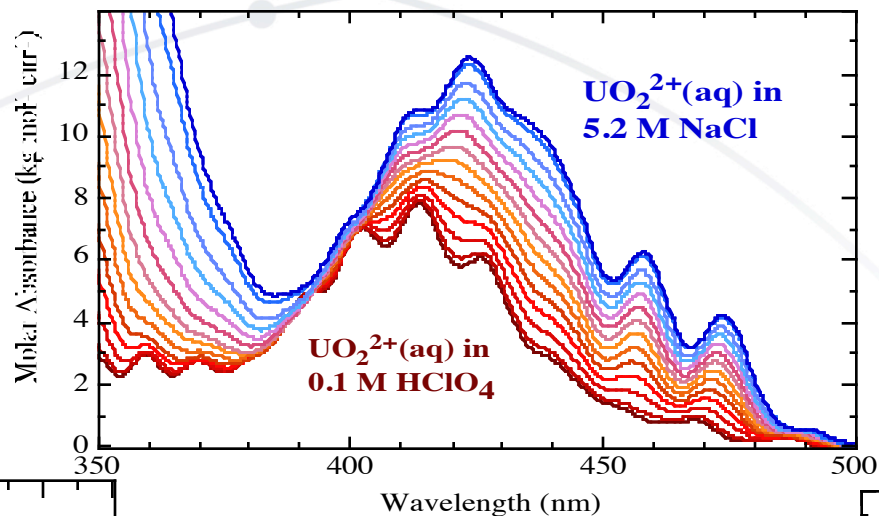
U(VI) in NaCl Solutions: FTIR Spectroscopy



U(VI) in NaCl Solutions: Raman Spectroscopy



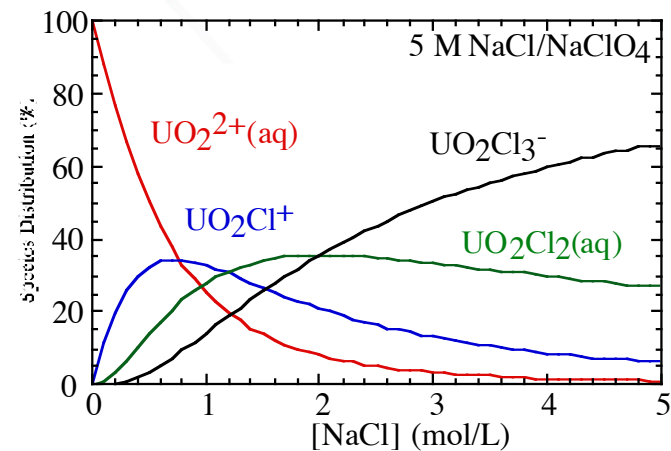
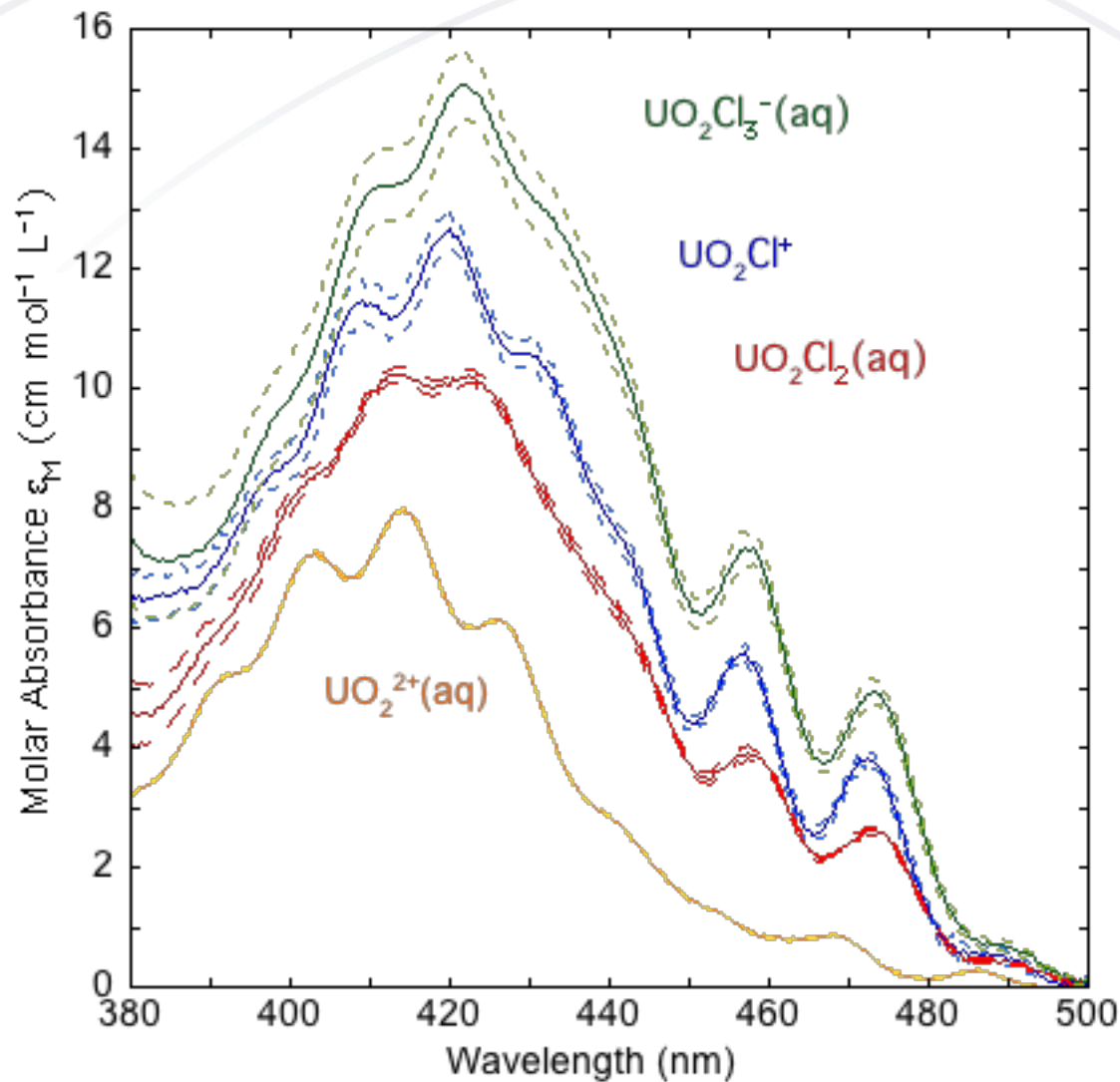
U(VI) in NaCl Solutions: UV-vis Absorbance



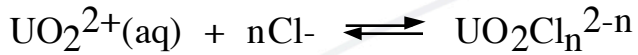
Runde et al., *Mat. Res. Soc. Symp. Proc.* **1997**, 465, 693-703.

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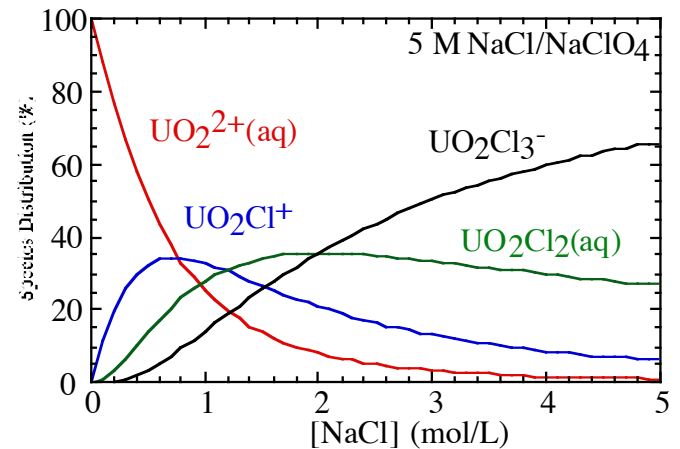
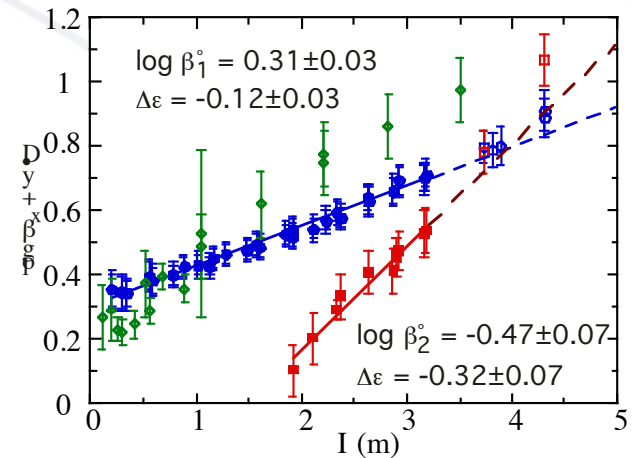
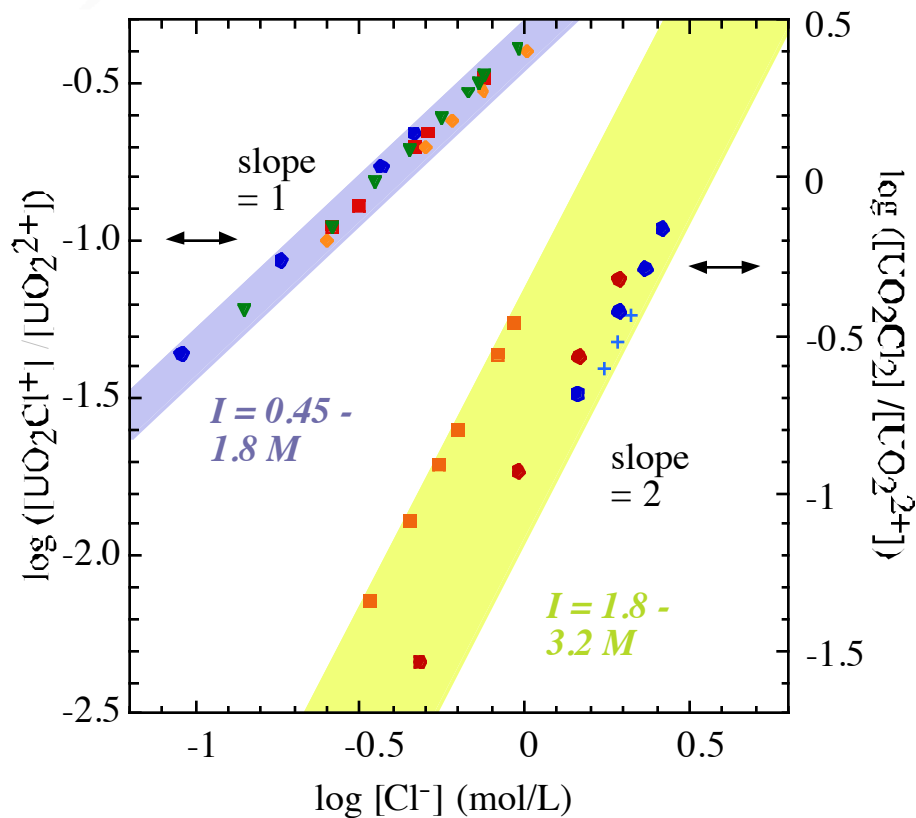
Single Component Spectra of $\text{UO}_2\text{Cl}_n^{2-n}$ ($n = 1, 2$)



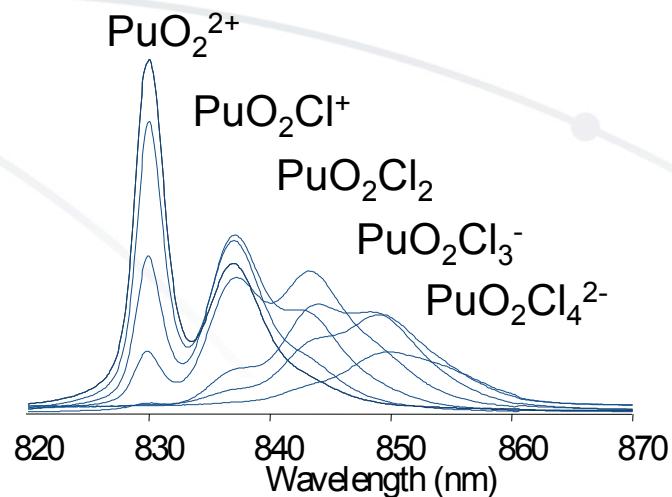
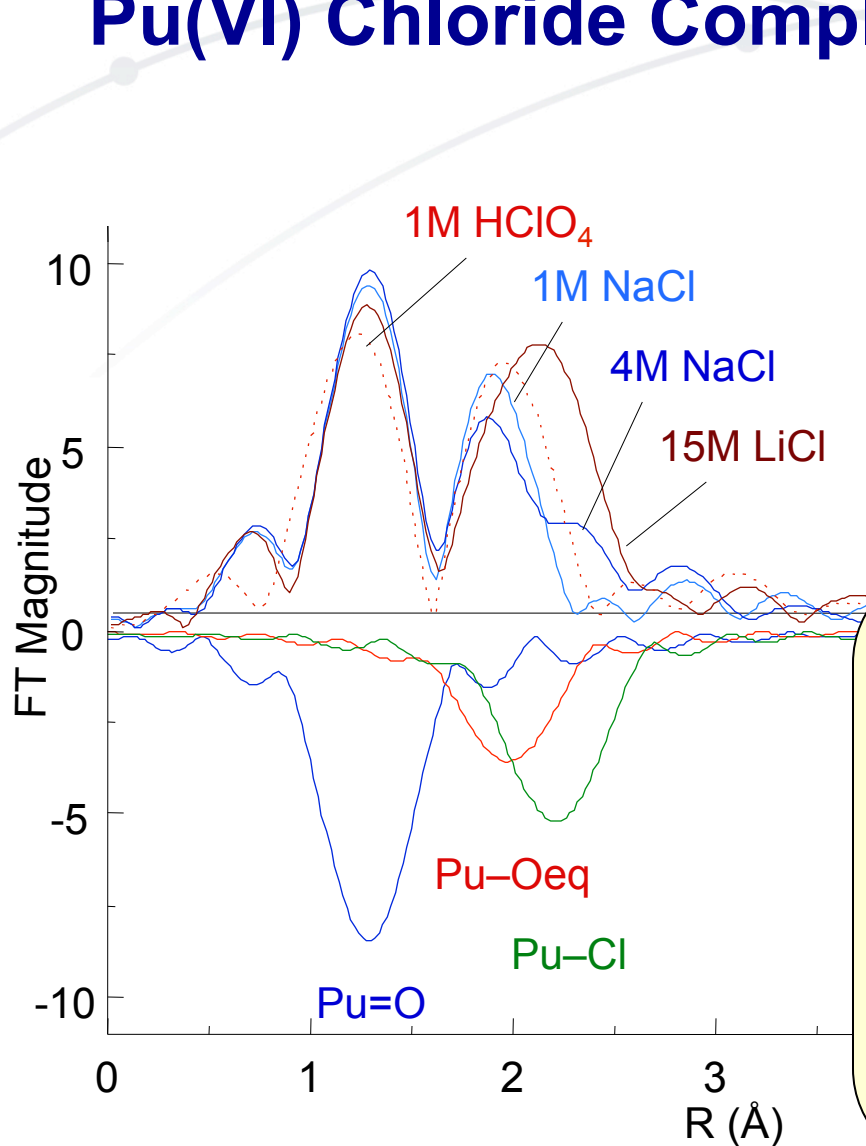
Thermodynamics of $\text{UO}_2\text{Cl}_n^{2-n}$ ($n = 1, 2$)



$$\log \beta_1 + 4 \cdot D = \log \beta_1^\circ - \Delta \varepsilon \cdot I_m$$



Pu(VI) Chloride Complexation

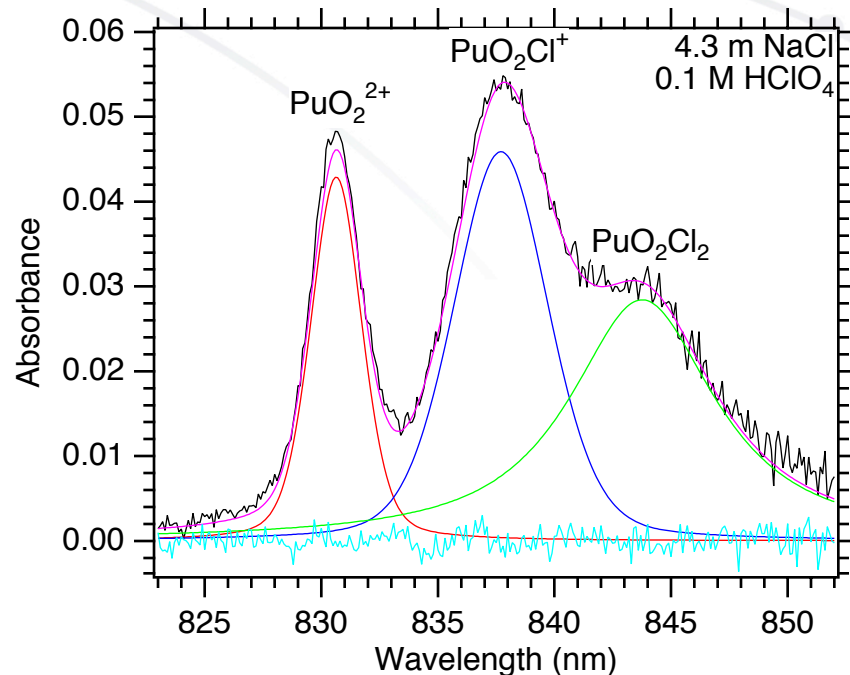
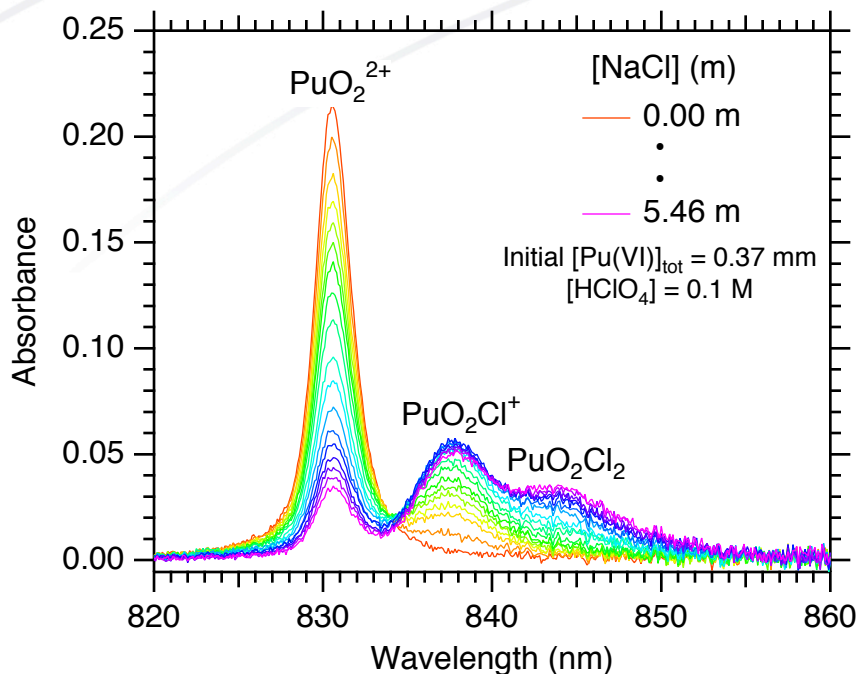


	1M	4M	15M [Cl ⁻]	PuO ₂ Cl ₄ ²⁻
Pu=O	1.74	1.75	1.75	1.737 (Å)
Pu-O _{eq}	2.40	2.43	-	(Å)
Pu-Cl	-	2.75	2.70	2.66 (Å)
	1M*	4M*	14M* [Cl ⁻]	UO ₂ Cl ₄ ²⁻
U=O	1.76	1.76	1.77	1.772 (Å)
U-O _{eq}	2.41	2.41	2.52	(Å)
U-Cl	-	2.71	2.73	2.68 (Å)

* Allen et al. *Inorg. Chem.* (1997) **36**, 4676.

Runde et al., *Mat. Res. Soc. Symp. Proc.* **1997**, 465, 693-703.

Pu(VI) Chloride Complexation

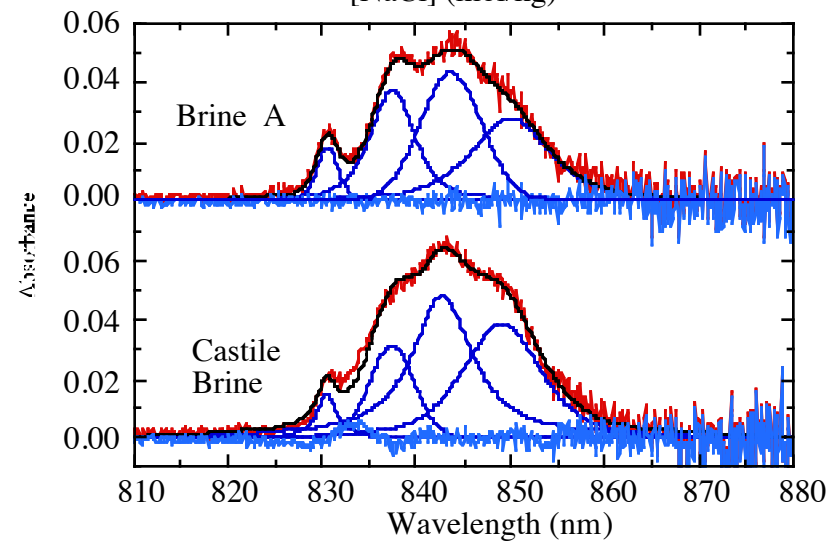
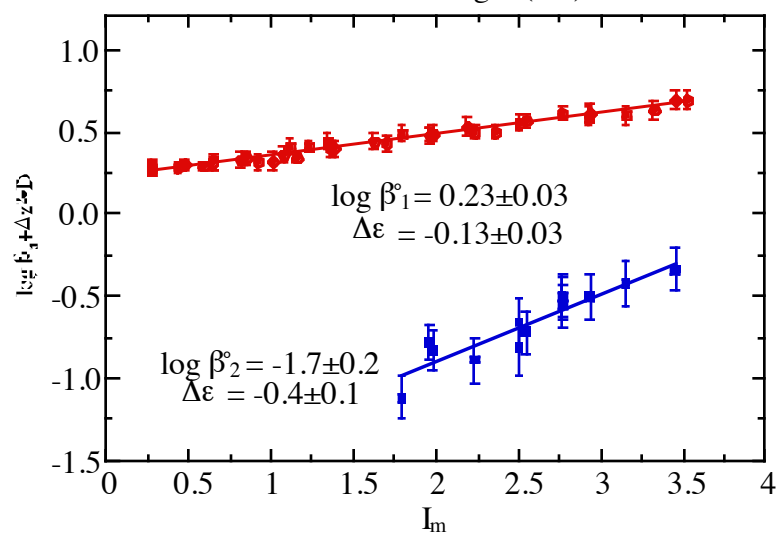
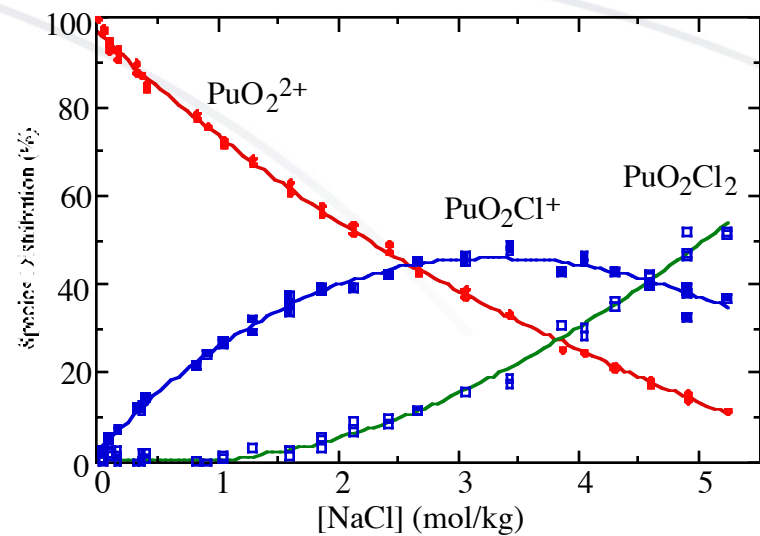
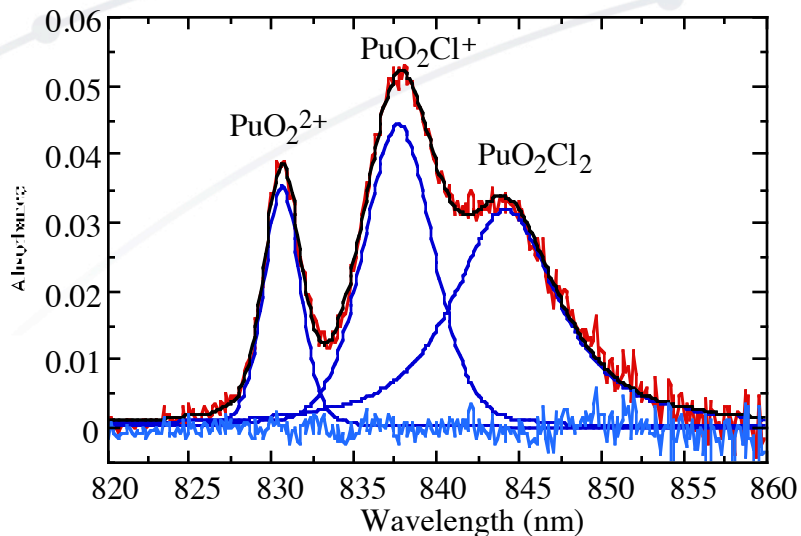


Pu(VI) Chloride Complex Stability Constants

	$\log \beta_q$ 1.0 M NaCl	$\log \beta_q$ 4.6 M NaCl	$\log \beta_q^\circ$
PuO_2Cl^+	-0.48 ± 0.03	-0.04 ± 0.05	0.23 ± 0.03
PuO_2Cl_2	—	-1.3 ± 0.3	-1.07 ± 0.2

Runde, W.; Reilly, S. D.; Neu, M. P. *Geochim. Cosmochim. Acta* **1999**, *63*, 3443-3449.

Pu(VI) in NaCl Solution



Runde, Reilly, and Neu. *Geochim. Cosmochim. Acta* **1999**, 63, 3443-3449

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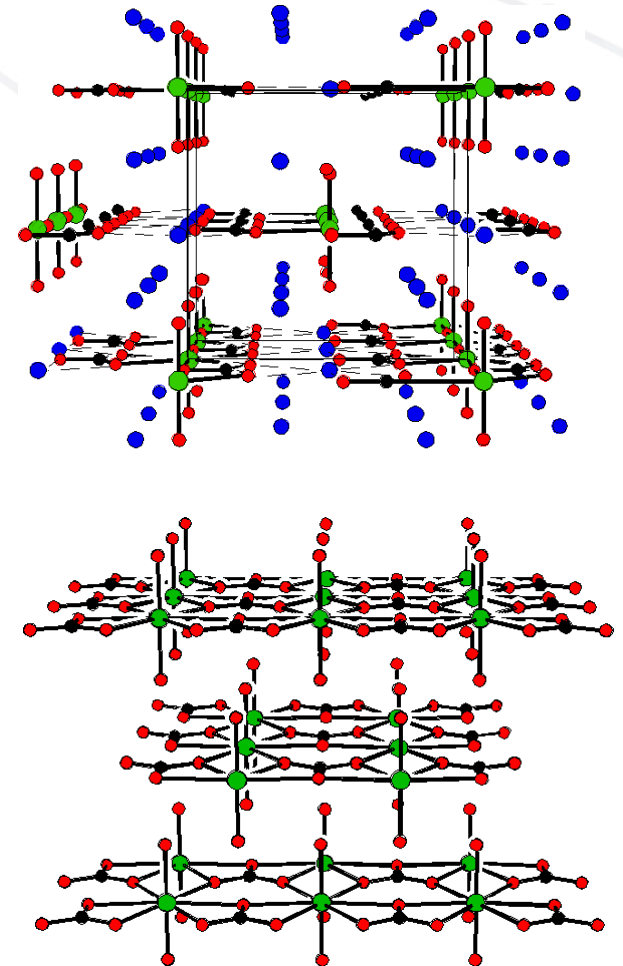
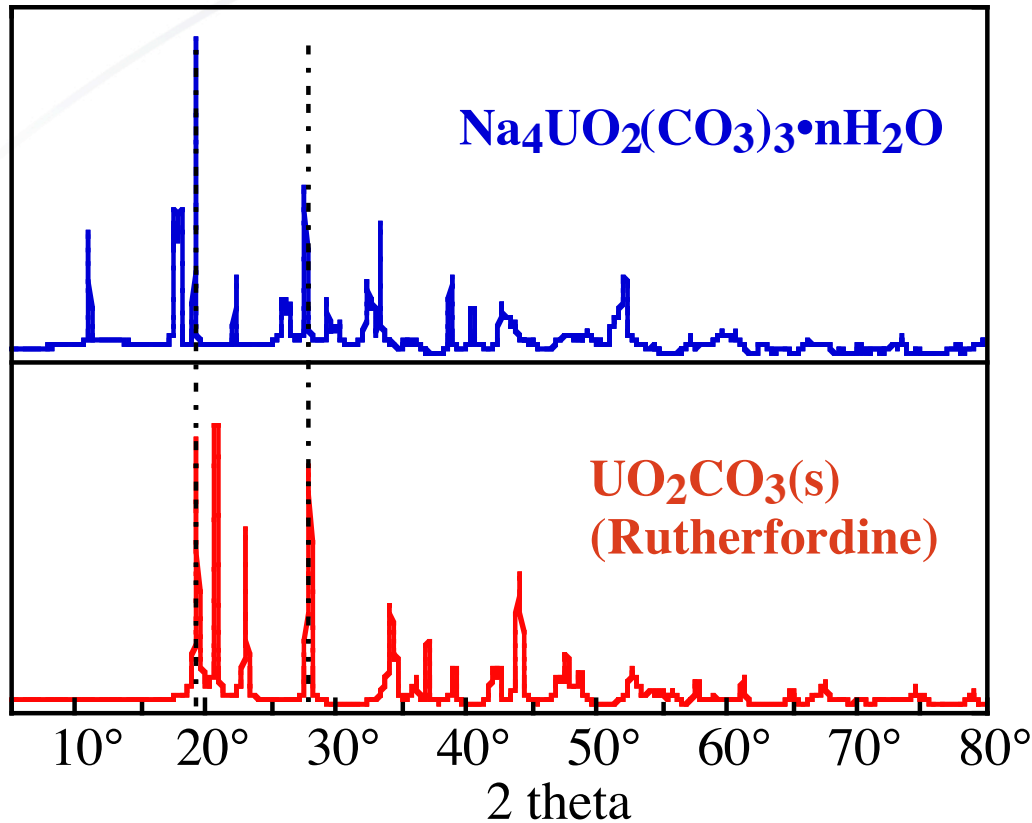


Actinide Solubility Behavior in Chloride:

An = U, Np, Pu

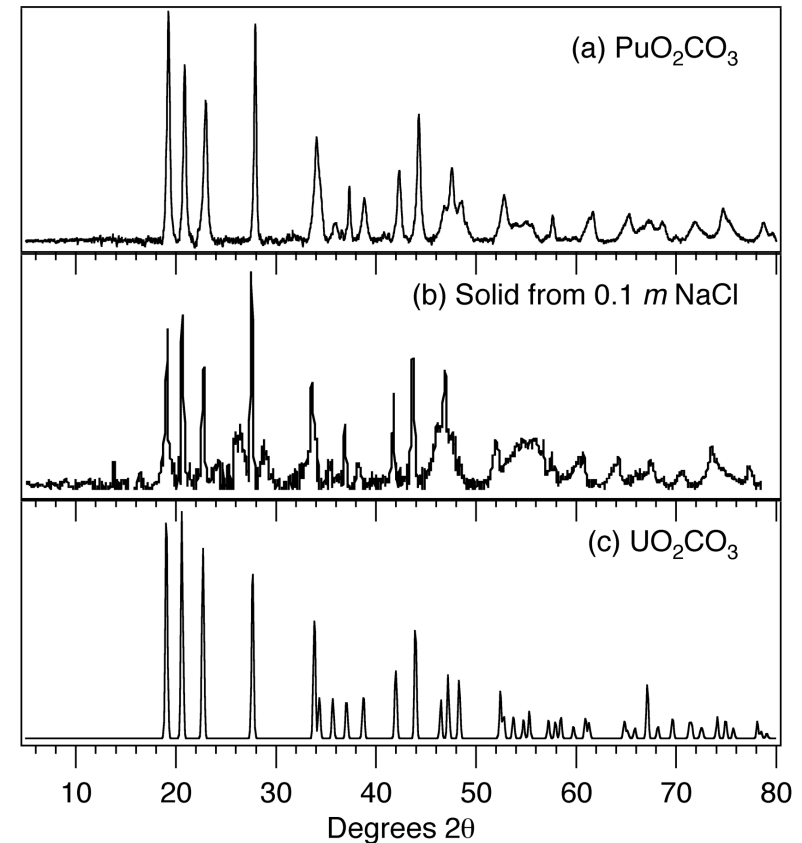
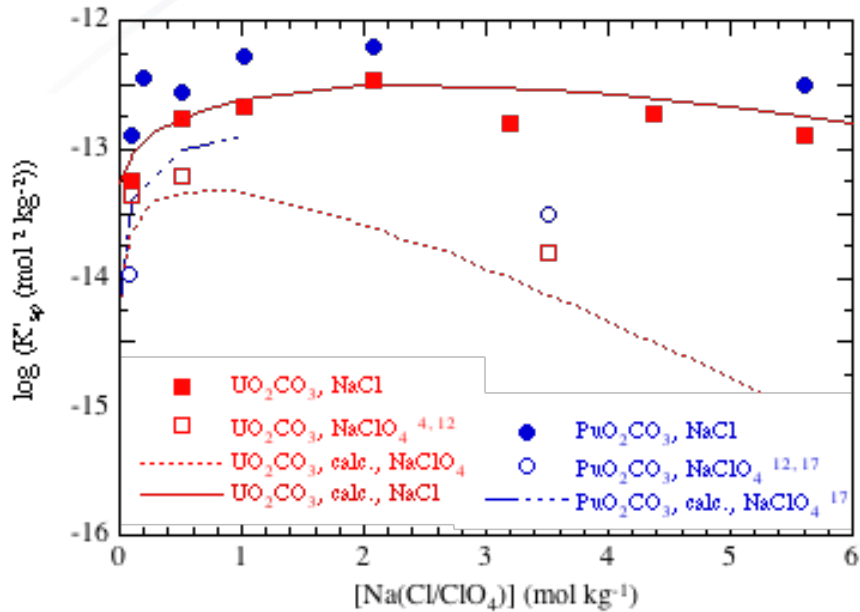
Uranium(VI) Carbonate Solids in NaCl

XRD



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AnO₂CO₃(s) Solubility in NaCl (An = U, Pu)



Reilly, Runde, and Neu, *Geochim. Cosmochim. Acta* **2007**, 71, 2672-2679.

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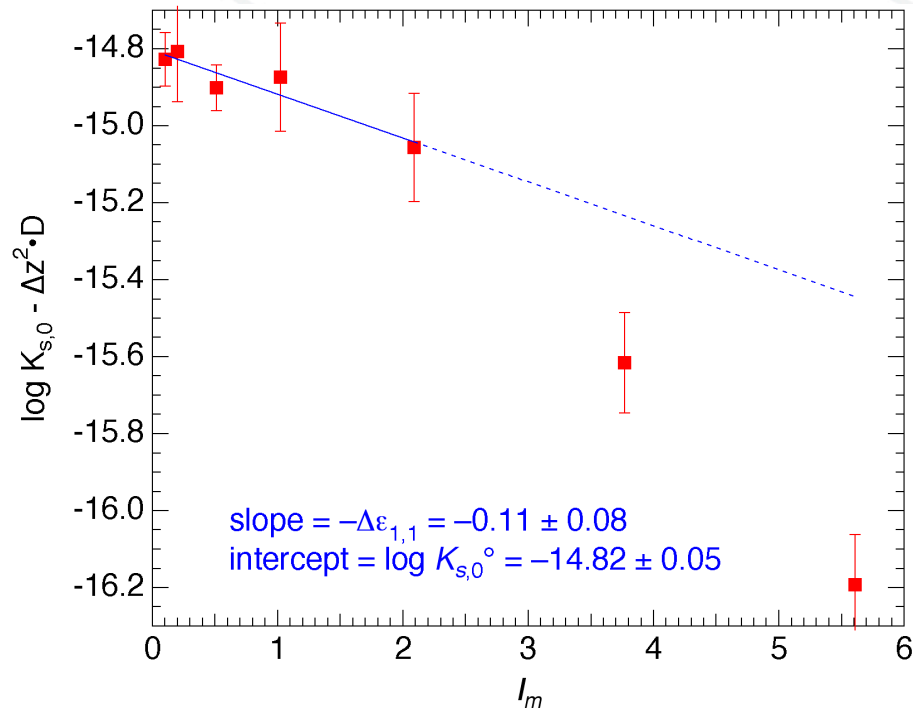
Solubility Product of $\text{PuO}_2\text{CO}_3(\text{s})$



Specific ion interaction theory (SIT) allows an apparent solubility product $K_{s,0}$ determined in an ionic medium of up to 3.5 m in ionic strength to be corrected to its thermodynamic value $K_{s,0}^\circ$ at zero ionic strength¹:

$$\log K_{s,0} - \Delta z^2 D = \log K_{s,0}^\circ - \Delta \epsilon_{1,1} I_m$$

← Apparent Solubility Product
 ← $\sum z_{\text{prod}}^2 - \sum z_{\text{react}}^2$ (+8)
 ← Debye-Hückel term
 ← Ion interaction coefficient
 ← Molal ionic strength



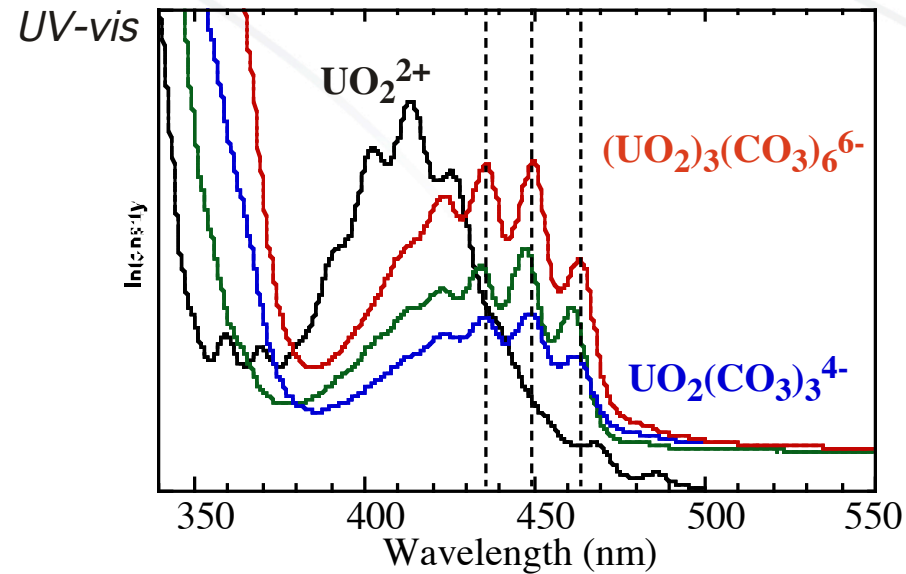
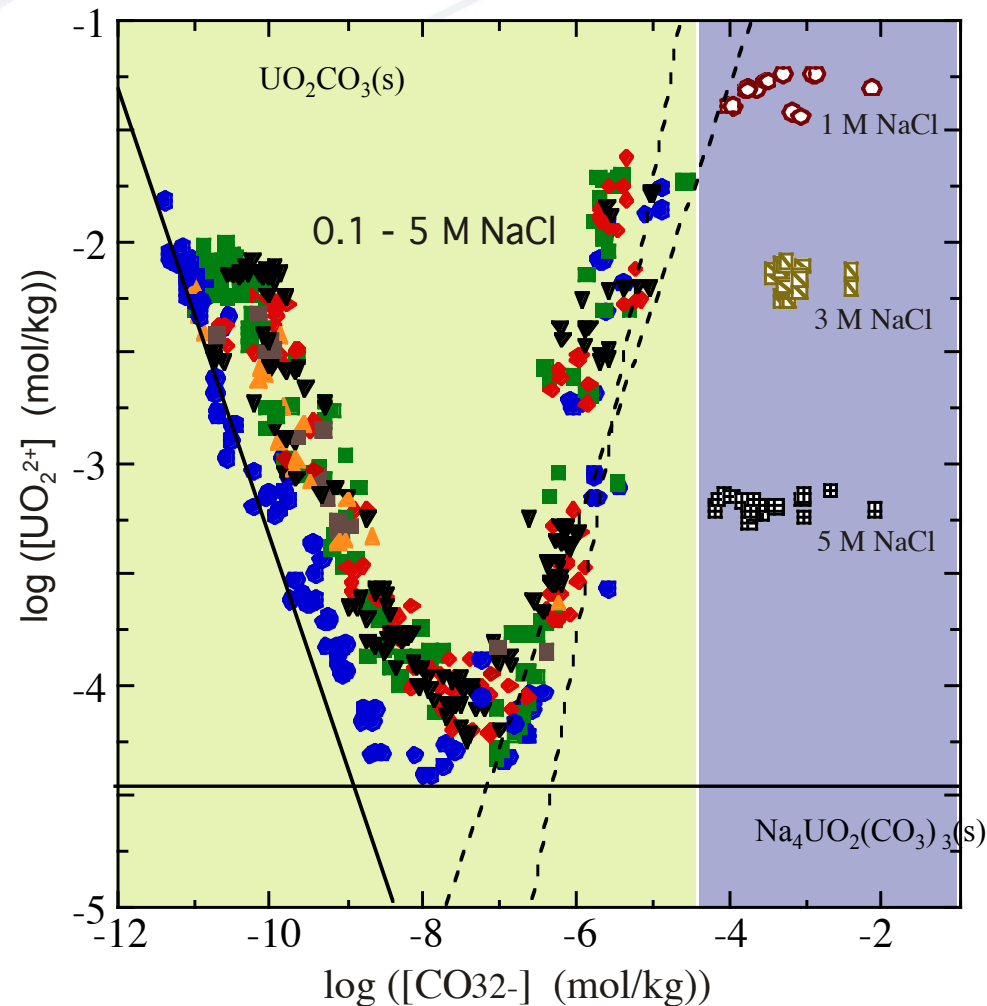
	Reilly et al.	OECD ¹
$\log K_{s,0}^\circ$	-14.82 ± 0.05	-14.65 ± 0.47
$\epsilon(\text{PuO}_2^{2+}, \text{Cl}^-)$	0.19 ± 0.09	— ²

¹ Guillaumont, R. et al. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium; Elsevier: Amsterdam, 2003; Vol. 5.

² $\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) = 0.21 \pm 0.21$, $\epsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) = 0.46 \pm 0.05$ (ref 1).

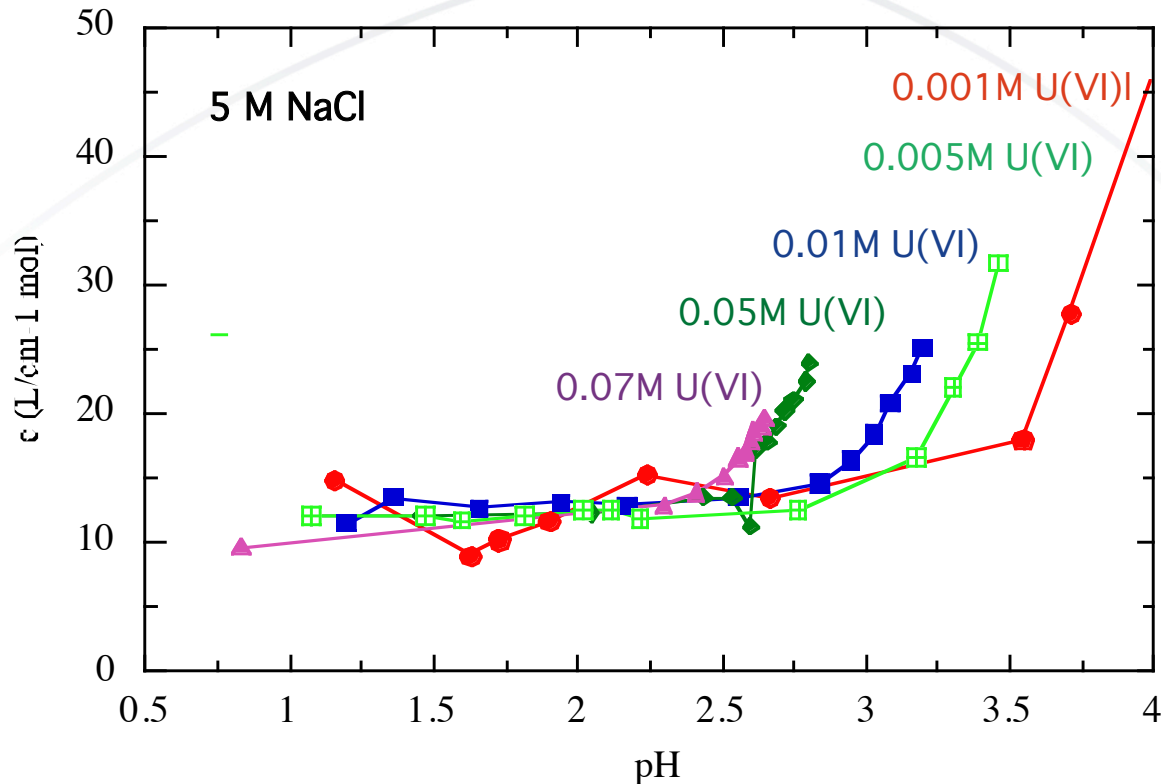
Reilly, Runde, and Neu, *Geochim. Cosmochim. Acta* **2007**, *71*, 2672-2679.

Uranium(VI) Carbonate Solubility in NaCl



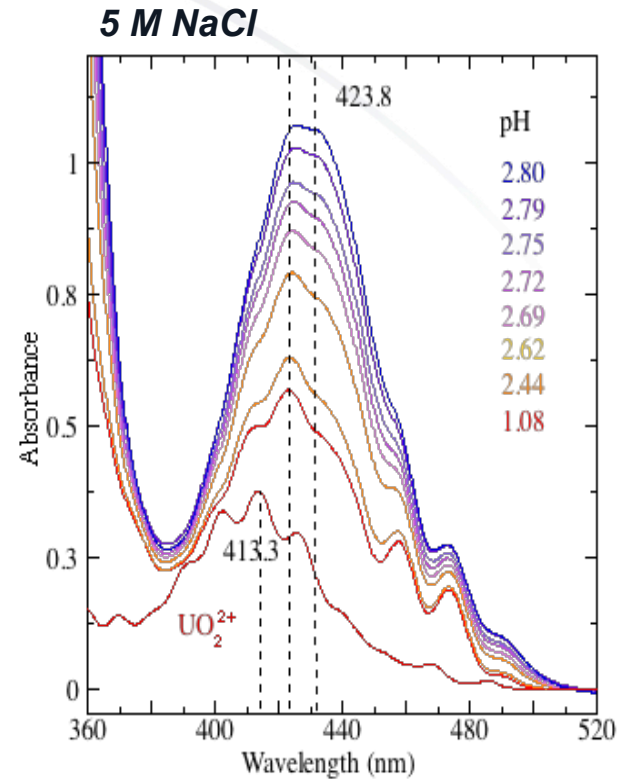
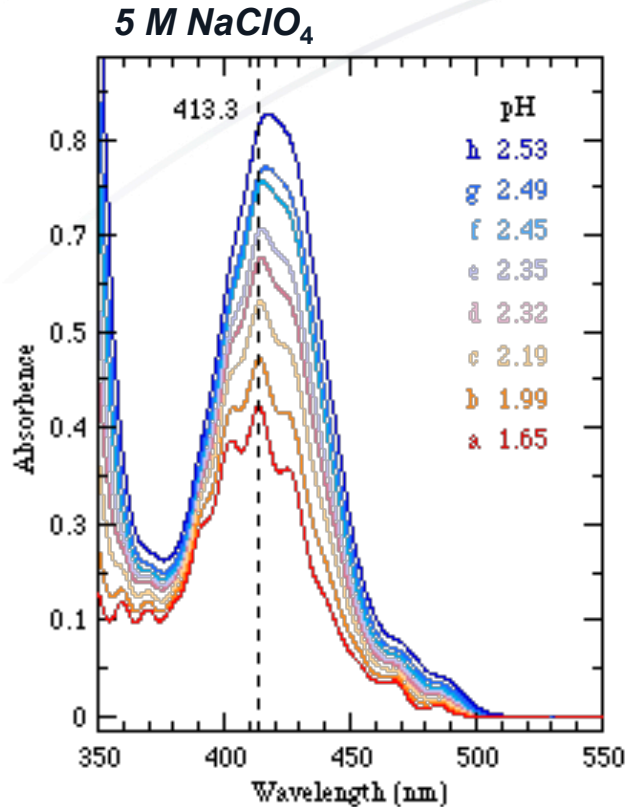
- Monomeric and polynuclear U(VI) solution species
- Two solid U(VI) carbonate phases
- Lower solubility at low NaCl conc.

Impact of U(VI)-Cl Interactions on Hydrolysis (1)



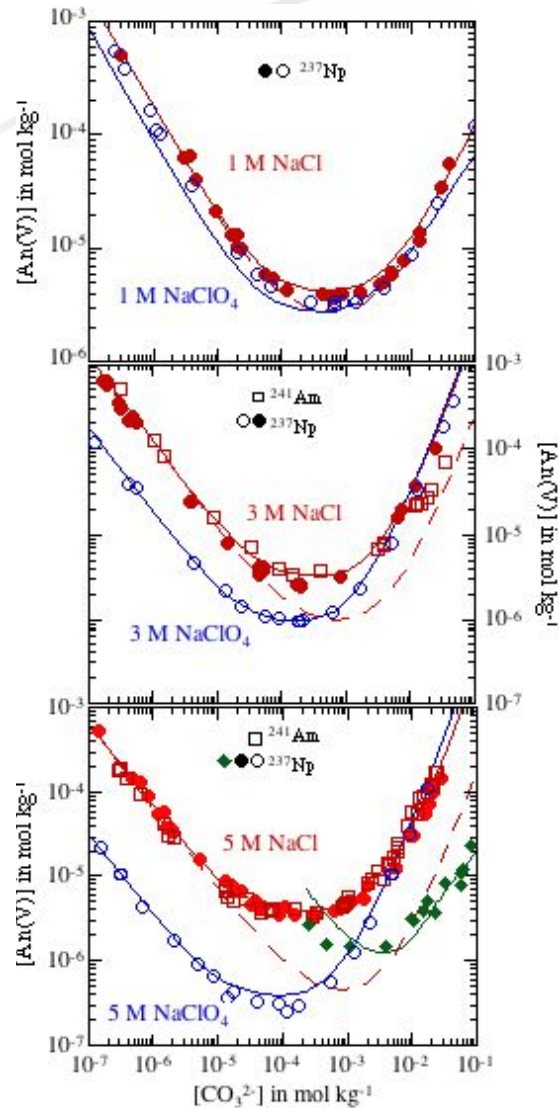
- Increasing [U(VI)] shifts hydrolysis edge to lower pH at conc. NaCl
- $(\text{UO}_2)_2(\text{OH})_2^{2+}$ found in NaClO_4 and in dilute NaCl.
- $(\text{UO}_2)_3(\text{OH})_5^+$ dominates over dimeric species in conc. NaCl.

Impact of U(VI)-Cl Interactions on Hydrolysis (2)



Absorbance maximum of U(VI) in conc. NaCl remains at shifted wavelength indicating chloride interaction.

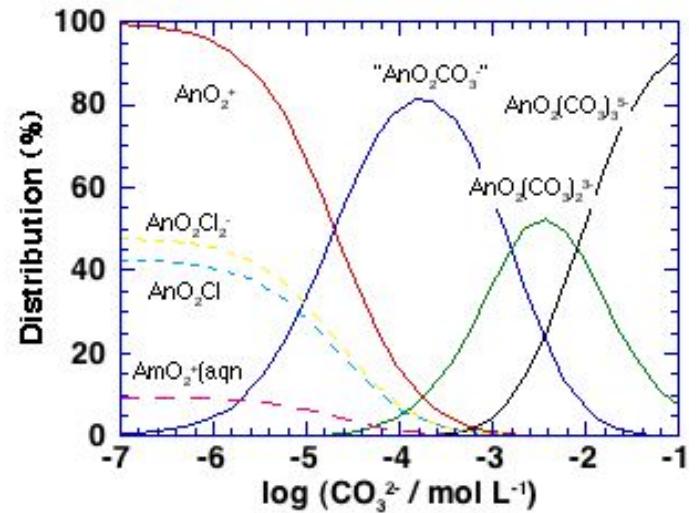
Impact of Cl on Np(V) Carbonate Solubility



- Tenfold higher solubility of An(V) in 5 M NaCl where $\text{NpO}_2(\text{H}_2\text{O})_5^+$ and $\text{NpO}_2(\text{H}_2\text{O})_3\text{CO}_3^-$ are present

- Similar solubility of An(V) at high carbonate: presence of limiting complex, $\text{NpO}_2(\text{CO}_3)_2^{5-}$

Slope analysis indicates both ionic strength effects and inner-sphere complexation of chloride

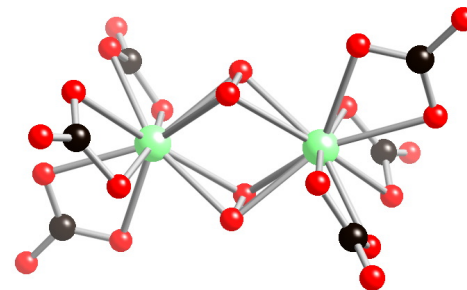
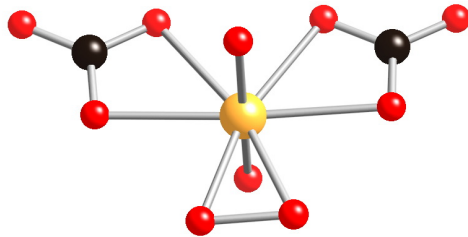


Solubility Data in NaClO_4 : Neck et al., *Radiochim. Acta* **1994**, 65, 29-37.

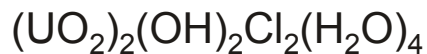
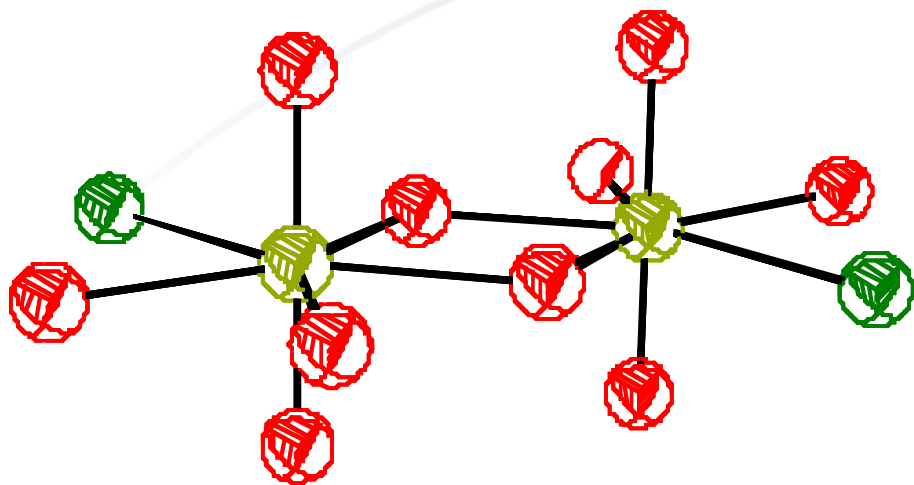
Solubility Data in NaCl : Runde et al., *Geochim. Cosmochim. Acta* **1996**, 60, 2065-2073.

Proposed and Verified Ternary Complexes (Examples)

- Low concentration of AmOHCO_3 (aq) (Bernkopf et al.)
- Mixed OH- CO_3 complexes verified spectroscopically and structurally for U(VI) and were proposed for Pu(IV)
- Ternary Humate-OH and Humate-Carbonate complexes of Cm(III) (Panak et al.)
- Mixed Np(V) OH- CO_3 complexes spectroscopically verified (Neck et al.)
- Small amounts of peroxide replace carbonate ligands to form $\text{UO}_2(\text{O}_2)(\text{CO}_3)_2^{4-}$ and dimeric $(\text{UO}_2)_2(\text{O}_2)(\text{CO}_3)_4^{6-}$ in solution
- Peroxide forms also ternary complexes with Pu(IV) and Pu(VI)



Mixed-Ligand Complexes in Solid State

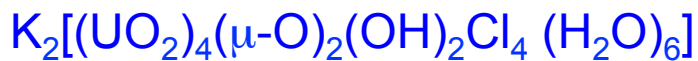


Åberg, *Acta Chem. Scand.* **23** (1969), 791-810.

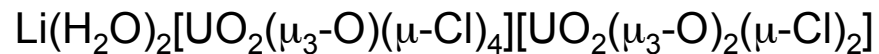
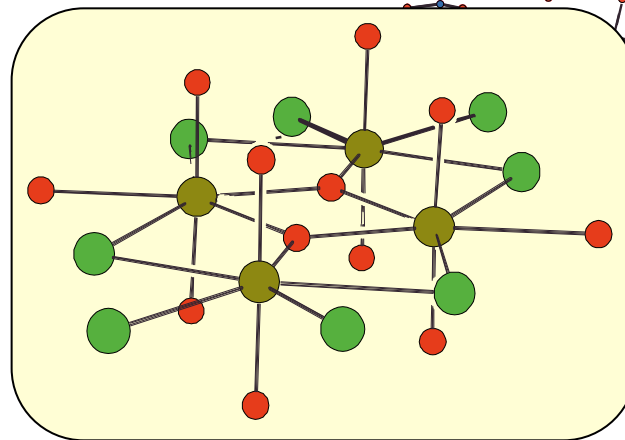
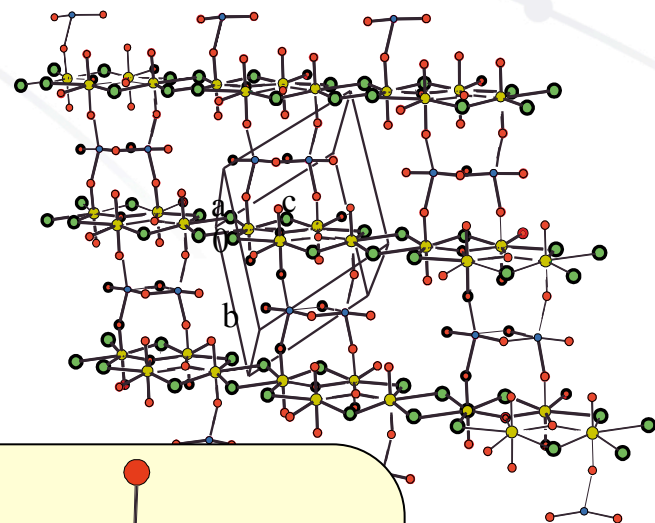
Other Examples:



(Bean et al. 2002)



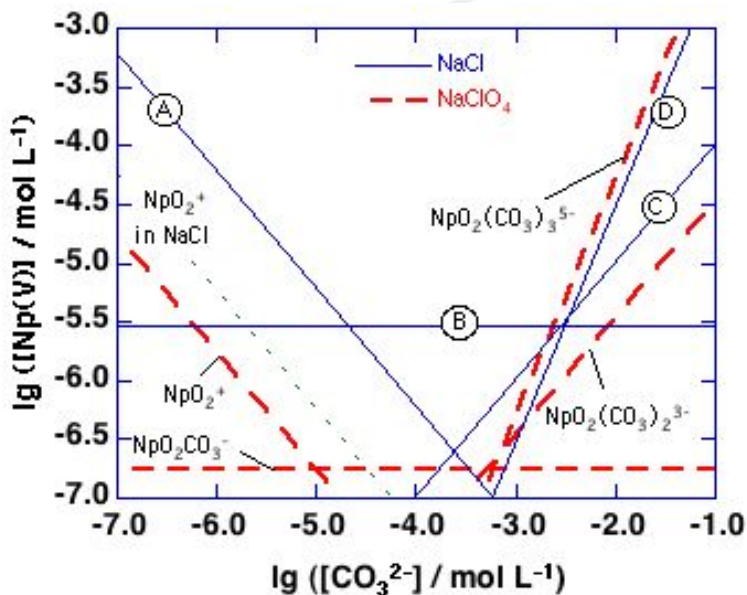
(Perrin, 1977)



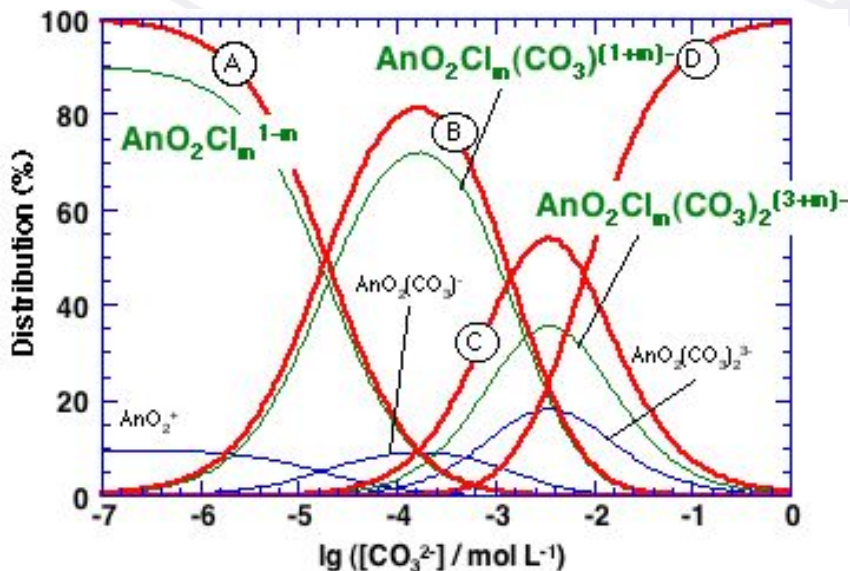
Bean et al. *Inorg. Chem.* **2002**, *41*, 6775-6779.

Formation of Ternary Np(V)-Cl-CO₃ Complexes?

A,B,C,D: Binary Np(V) Carbonate Species



A,B,C,D: Slopes for $\text{NpO}_2(\text{CO}_3)_n^{(1-2n)}$ ($n=0-3$)

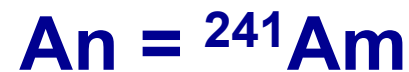


red: Distribution for $\text{NpO}_2(\text{CO}_3)_n^{(1-2n)}$ ($n=0-3$) in NaClO_4
 blue: Distribution for $\text{NpO}_2(\text{CO}_3)_n^{(1-2n)}$ ($n=0-3$) in NaCl
 green: Np(V) Cl-CO₃ complexes in NaCl

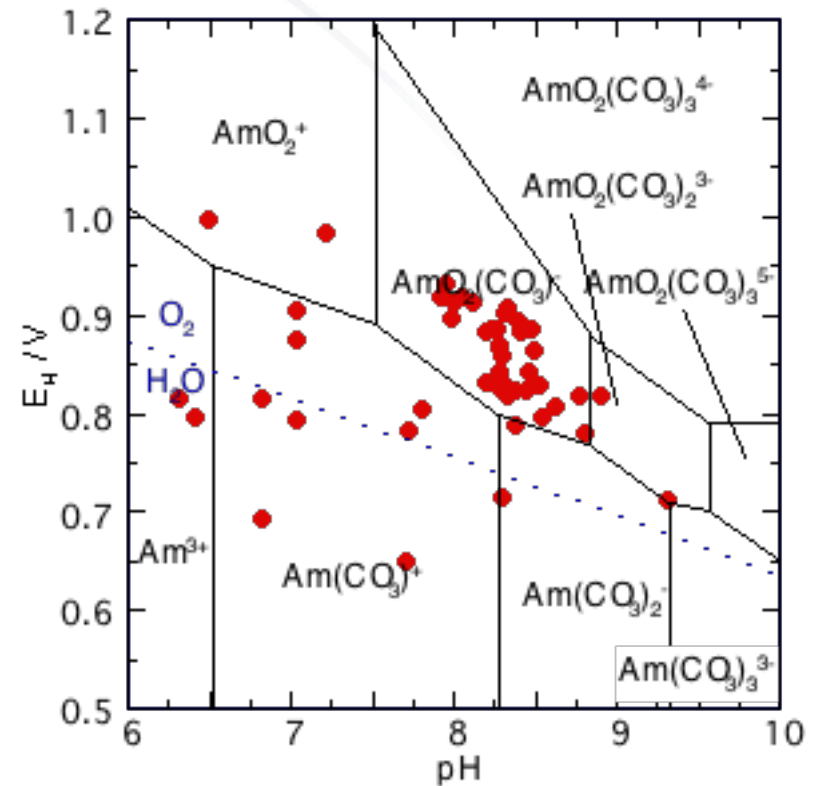
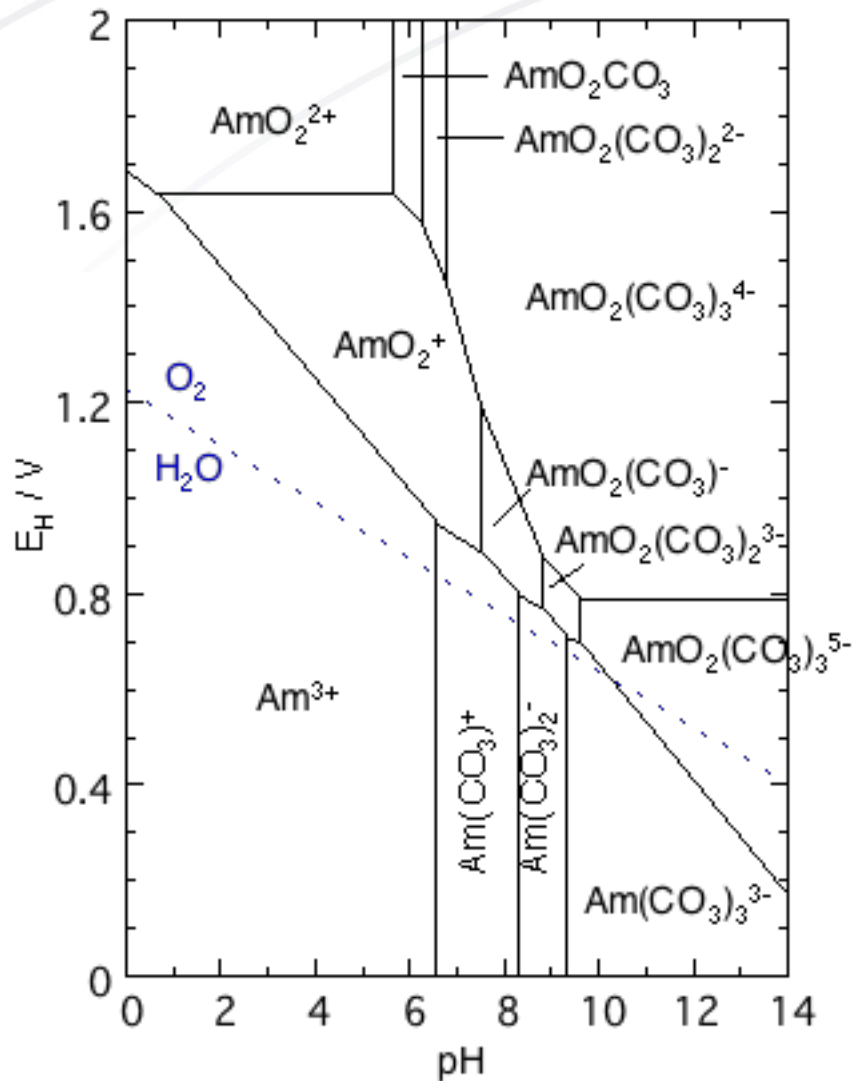
- Solubility differences for NpO_2^+ (and $\text{NpO}_2\text{CO}_3^-$) in NaCl and NaClO_4 are comparable
- Solubility difference for $\text{NpO}_2(\text{CO}_3)_2^{3-}$ in NaCl and NaClO_4 is much smaller, diminishes for $\text{NpO}_2(\text{CO}_3)_3^{5-}$
- Solubility difference for $\text{NpO}_2(\text{CO}_3)_2^{5-}$ in NaCl and NaClO_4 is ionic strength effect
- Small spectroscopic shifts and slope analysis of solubility data suggest mixed Np(V)-Cl-CO₃ complexes



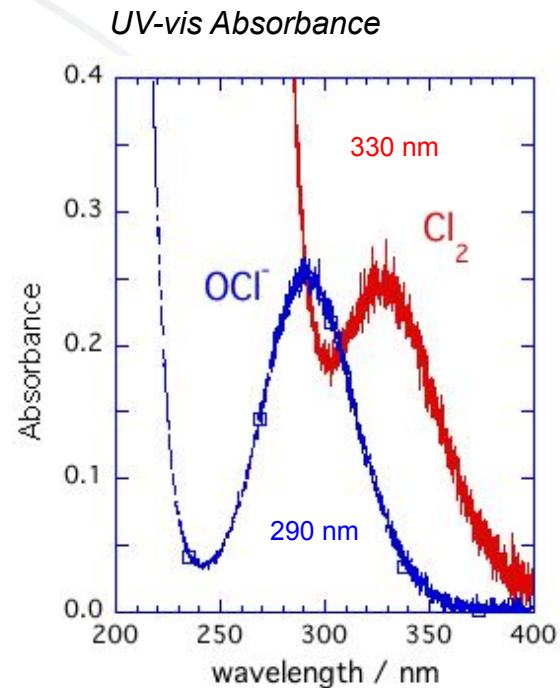
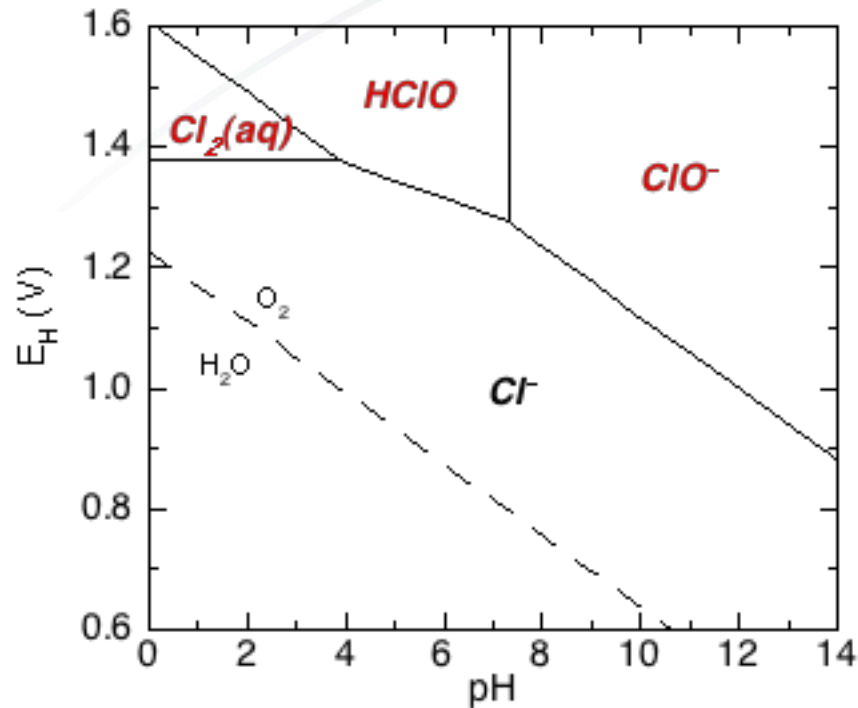
Self-Induced Radiolysis of Actinides in Chloride:



Radiolysis: Pourbaix Diagram of Americium



Radiolysis: Formation of Oxidizing Species



Oxidizing Cl-Species observed spectroscopically

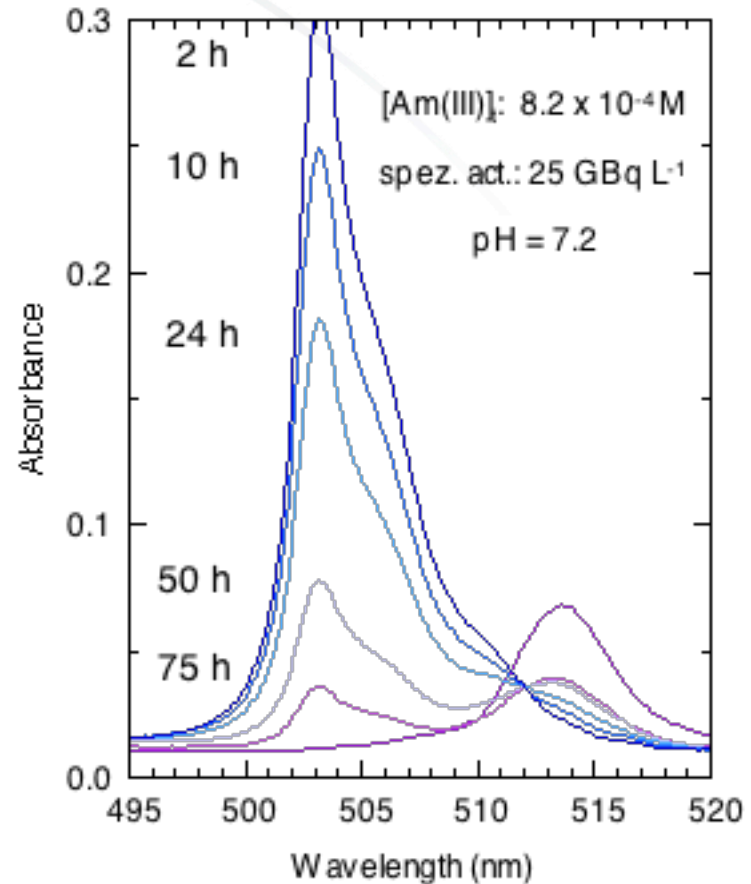
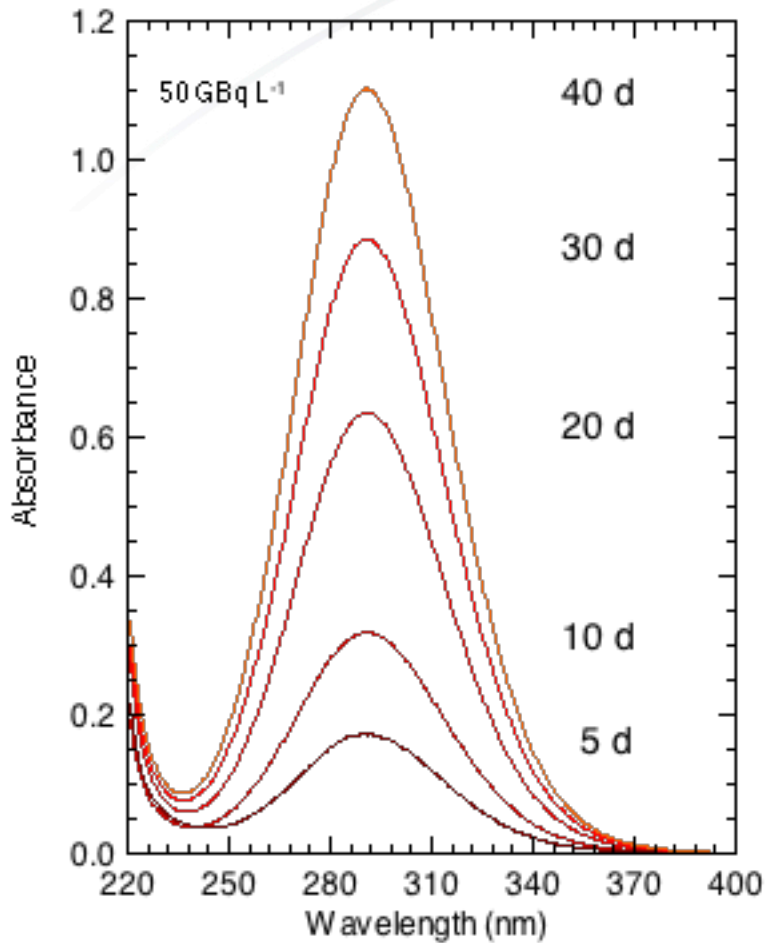
Cl_2 formation at acidic pH; OCl^- forms at near-neutral pH

Runde and Kim. *RCM-01094*, 1994.

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Radiolysis: Self-Induced Radiolysis of Am(III)



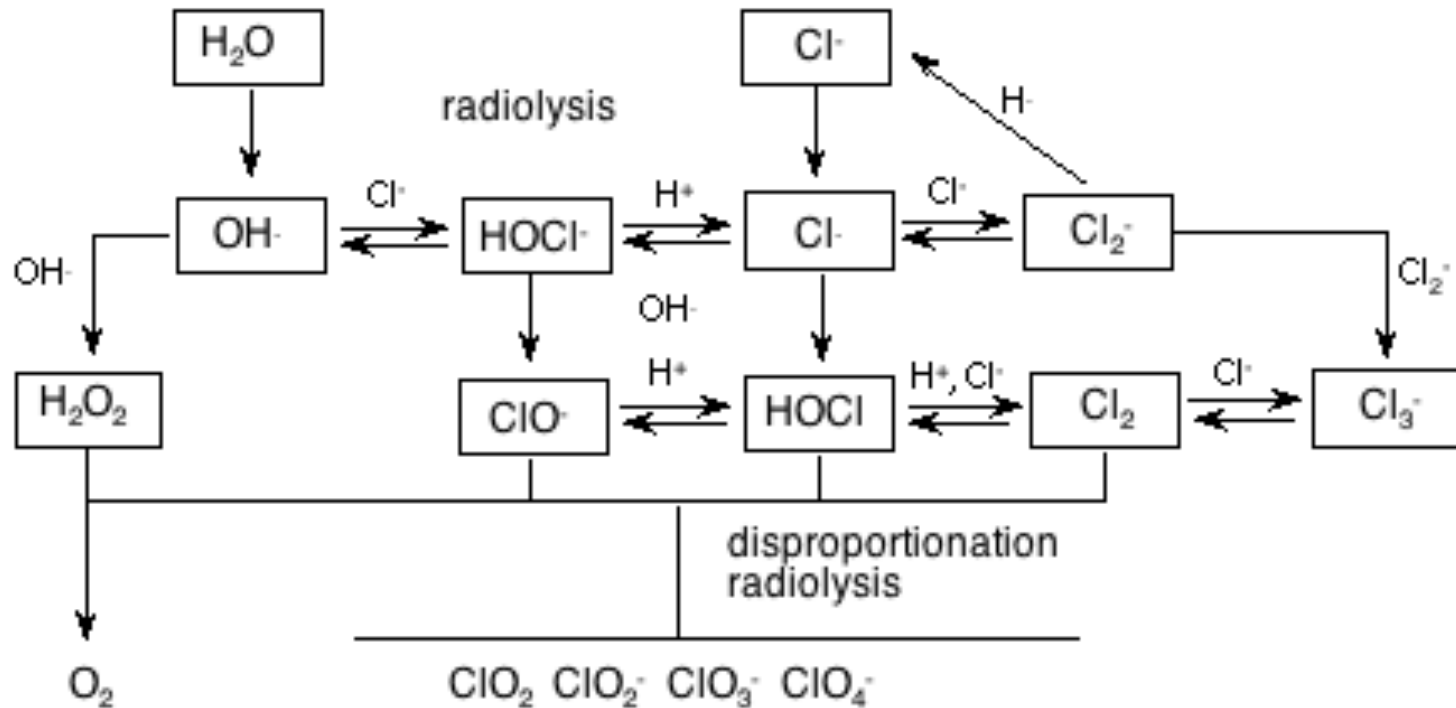
Runde and Kim. *RCM-01094*, 1994.

UNCLASSIFIED

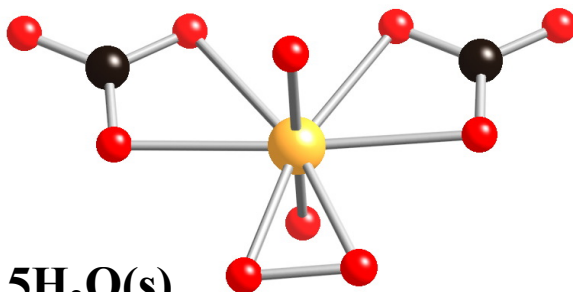
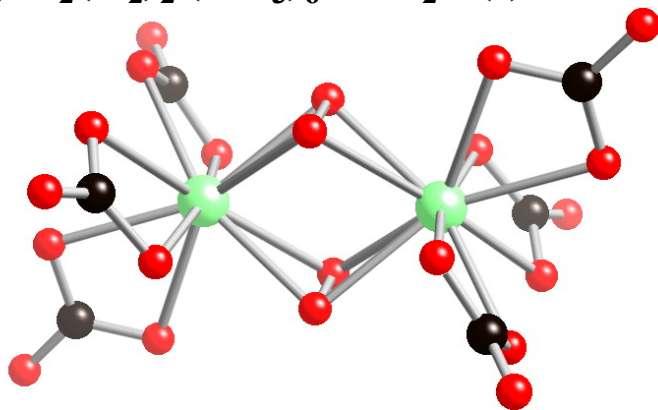
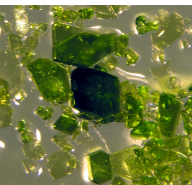
Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

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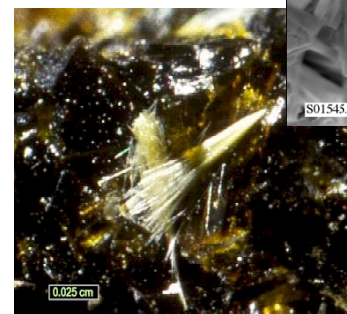
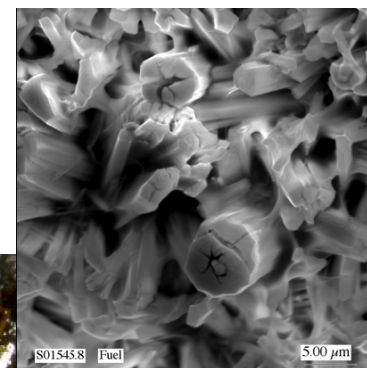
Radiolysis: Radiolysis Reactions



Subsequent Interactions with Radiolysis Products (i.e. H_2O_2) in Aqueous Solutions



Uranium peroxide (studtite) has been identified as Spent Nuclear Fuel alteration Phase.



Buck et al., Report PNNL-14277 (2003).

Zehnder et al. *Acta Cryst.* **2005**, C61, i3.

Runde, W. et al. *Chem. Comm.* **2007**, 17, 1728-1729.

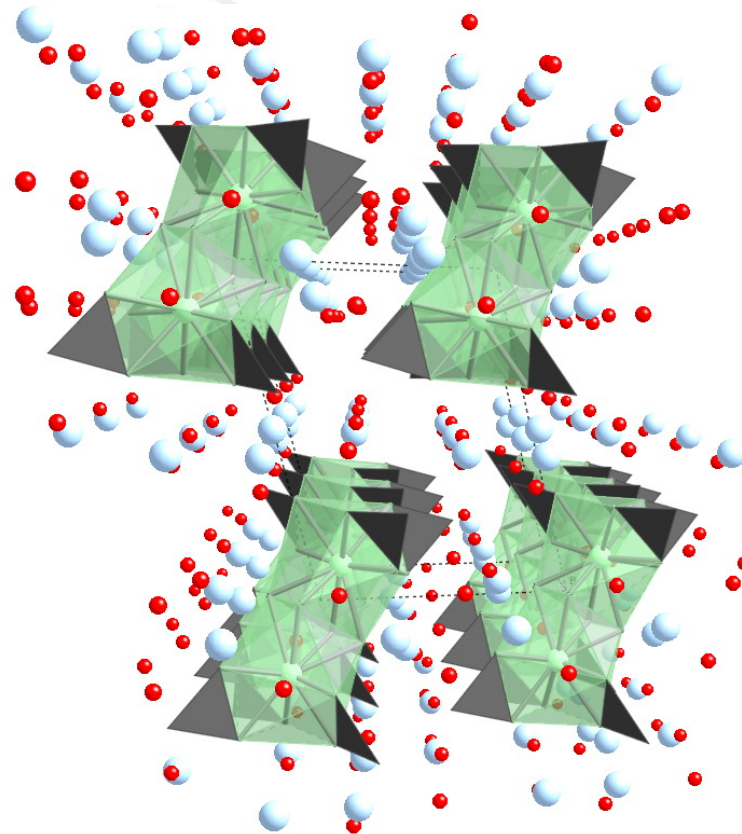
An(V,VI) Chloride Coordination: Summary

- Chloride has been shown to replace water molecules for inner-sphere coordination with An(V) and An(VI), but will not replace hydroxide or carbonate.
- UO_2^{2+} does not interact with ClO_4^- ions, but Cl^- ions form inner-sphere complexes. UO_2Cl^+ and UO_2Cl_2 are the predominant U(VI) chloro species in acidic NaCl solution (up to 5m).
- $\text{AnO}_2\text{X}_4^{2-}$ has been isolated from concentrated LiCl solutions (12m).
- Extraction (Neck *et al.*) and Spectroscopic data indicate weaker chloride complexation
- The solubility of Np(V) and U(VI) increases with NaCl concentrations, especially when $\text{AnO}_2^{2+/+}$, and $\text{AnO}_2\text{CO}_3^{0/-}$ are present.
- Spectroscopic data suggest the formation of mixed An(V,VI) Cl-OH and Cl- CO_3 species in concentrated NaCl solutions.
- Solubility and thermodynamic constants for An(V,Cl) (An=U, Np, Pu, Am) in NaCl have been determined considering chloride complexation

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