

**Structural and Thermodynamic
Evaluation
of Cerium(IV)
Hydroxypyridonate Complexes
as Models
for Plutonium(IV)
Complexation**

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Introduction

Treatment of mixed waste includes removal of *very low concentrations* of radioisotopes in the presence of *competing ions* such as Fe(III) and *strong chelating ligands* such as EDTA.

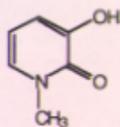
Rational design of powerful, highly selective sequestering agents involves careful *thermodynamic and structural characterization* of their complexes.

Non-radioactive lanthanides can be used as *models* for actinide complexation - e.g. Ce(IV) for Pu(IV).

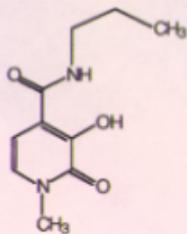
Goals

- **Synthesis of new metal ion-specific ligands**
- **Structural and thermodynamic investigation of these ligands and their complexes with relevant metal ions**
- **Development of sequestering agents based on these ligands, and their incorporation into systems designed to be prototypes of inexpensive and highly effective materials for hazardous metal decontamination**

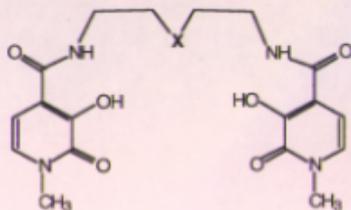
Me-3,2-HOPO Ligands of Various Denticity



Me-3,2-HOPO, HL¹

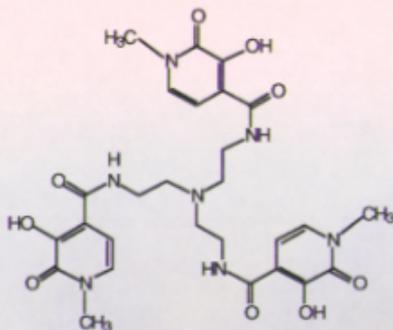


PR-Me-3,2-HOPO, HL²

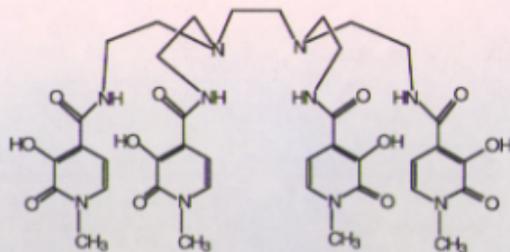


5LI-Me-3,2-HOPO (X = CH₂), H₂L³

5LIO-Me-3,2-HOPO (X = O), H₂L⁴

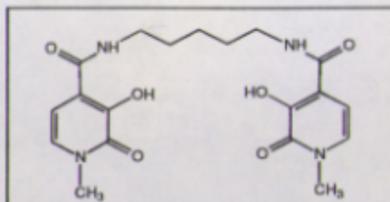
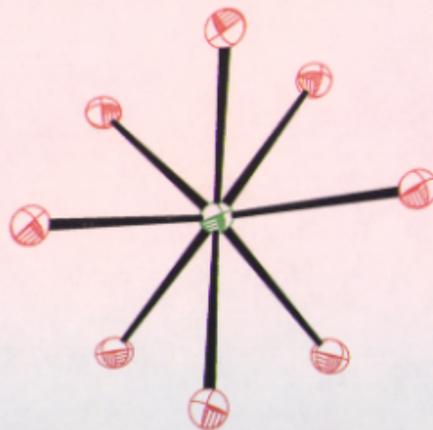
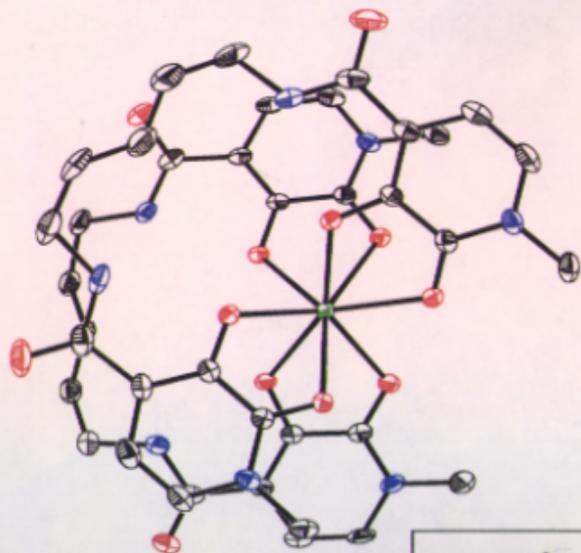


TREN-Me-3,2-HOPO, H₃L⁵

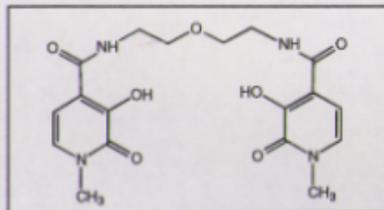
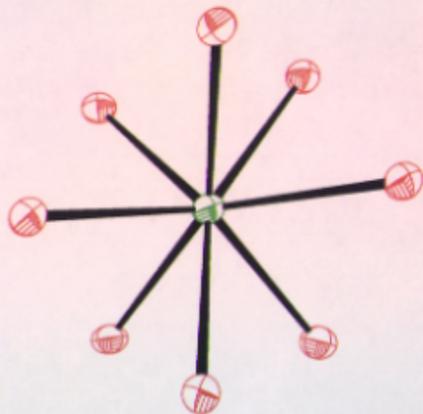
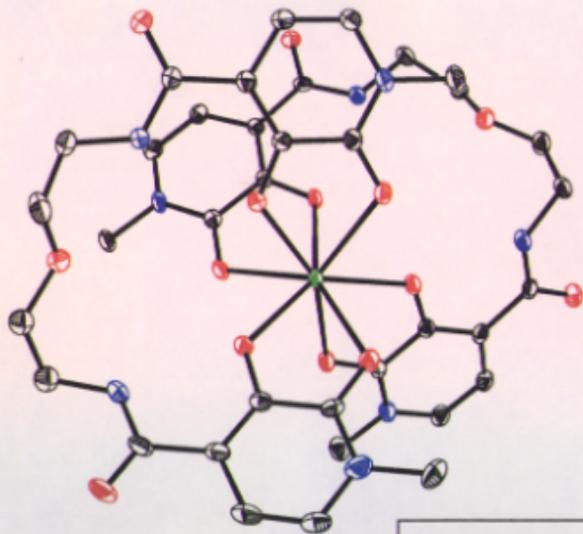


H(2,2)-Me-3,2-HOPO, H₄L⁶

Crystal Structure of Ce(IV)-5LI-Me-3,2-HOPO (top view)

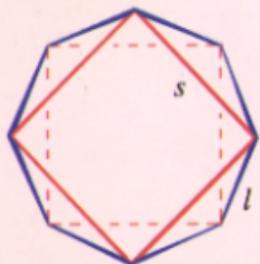


Crystal Structure of Ce(IV)-5LIO-Me-3,2-HOPO (top view)



Hard Sphere Models (HSM) of Eight Coordinate Polyhedra

D_{4d}



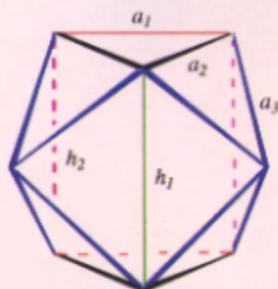
$$s = l = 1.215 r$$

dihedral angle along:

$$s: 103.84^\circ$$

$$l: 127.5^\circ$$

C_{2v}



$$h_1 = h_2 = 1.491 r$$

$$a_1 = a_2 = a_3 = 1.155 r$$

dihedral angle along:

$$a_1: 90^\circ$$

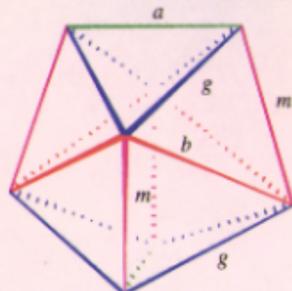
$$a_2: 131.8^\circ$$

$$a_3: 108.8^\circ$$

$$h_1: 158.2^\circ$$

$$h_2: 109.1^\circ$$

D_{2d}



$$a = m = g = 1.199 r$$

$$b = 1.499 r$$

dihedral angle along:

$$a: 128.74^\circ$$

$$b: 150.5^\circ$$

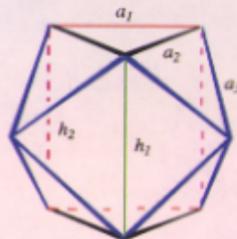
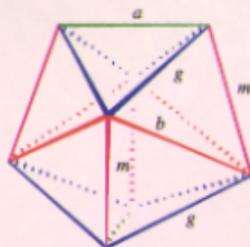
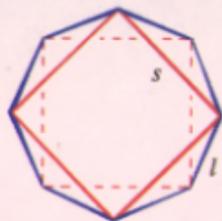
$$g: 117.53^\circ$$

$$m: 106.32^\circ$$

1. Hoard, J. I.; Silverton, J.V., *Inorg. Chem.*, **1963**, 2, 235.

2. Muettteries, E.L.; Guenzenberger, L.J., *J. Amer. Chem. Soc.*, **1974**, 96, 1748.

Coordination Polyhedron of Ce(IV)-5LI-Me-3,2-HOPO



Atoms defining plane	Distance
O(1)	0.099(3)
O(2)	-0.109(3)
O(5)	0.115(3)
O(6)	-0.101(3)

Atoms defining plane	Distance
O(7)	0.011(3)
O(8)	0.013(3)
O(11)	0.012(3)
O(12)	-0.012(4)

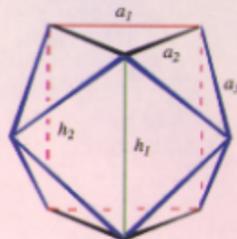
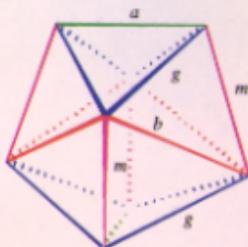
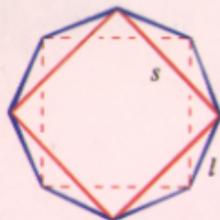
$$R = \frac{\sum || \delta_{\text{obs}} | - | \delta_{\text{calc}} ||}{\sum | \delta_{\text{obs}} |}$$

Square-antiprism
(HSM)
R = 0.039

Dodecahedron
(HSM)
R = 0.065

Bicapped Trigonal Prism
(HSM)
R = 0.145

Coordination Polyhedron of Ce(IV)-5LIO-Me-3,2-HOPO



Atoms defining plane	Distance
O(1)	0.227(4)
O(2)	-0.345(5)
O(6)	0.242(4)
O(7)	-0.238(4)

Atoms defining plane	Distance
O(8)	0.069(4)
O(9)	-0.108(5)
O(13)	0.094(4)
O(14)	-0.280(8)

$$R = \sum || \delta_{\text{obs}} | - | \delta_{\text{calc}} || / \sum | \delta_{\text{obs}} |$$

Square-antiprism
(HSM)
R = 0.070

Dodecahedron
(HSM)
R = 0.068

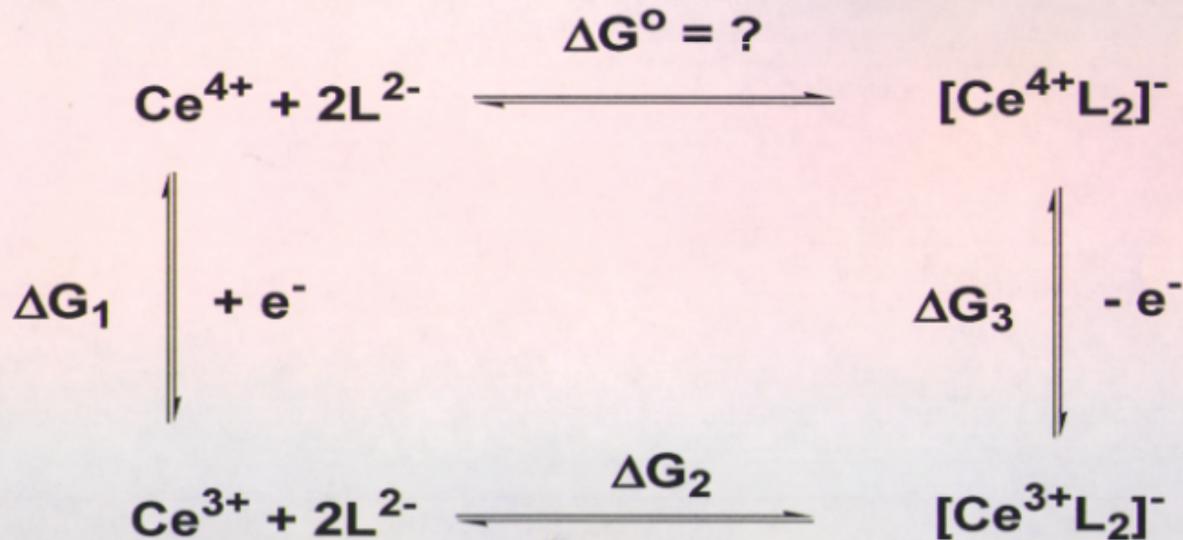
Bicapped Trigonal Prism
(HSM)
R = 0.150

Protonation Constants of Me-3,2-HOPO Ligands

Ligand	logKa1	logKa2	logKa3	logKa4	logKa5	logKa6	Mean*
Me-HOPO	8.82						
PR-HOPO	<u>6.12</u>						6.12
5LI-HOPO	<u>6.86</u>	<u>5.94</u>					6.40
5LIO-HOPO	<u>7.14</u>	<u>5.91</u>					6.53
TREN-HOPO	8.20	<u>6.95</u>	<u>5.80</u>	<u>4.96</u>			5.90
H(2,2)-HOPO	8.44	<u>7.38</u>	<u>6.57</u>	<u>5.88</u>	<u>4.94</u>	2.38	6.20

*per *amide*-HOPO group in the ligand (underlined values).
 The average of all underlined constants is 6.20.

Thermodynamic Cycle for Determination of Equilibrium Constants with Ce(IV)

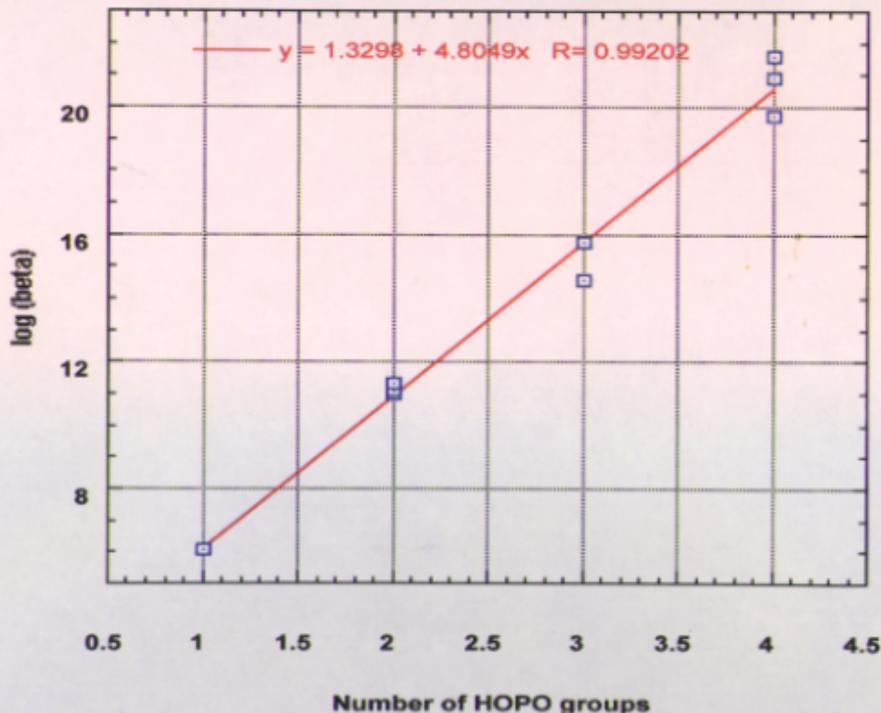


$$\Delta G^{\circ} = \Delta G_1 + \Delta G_2 + \Delta G_3$$

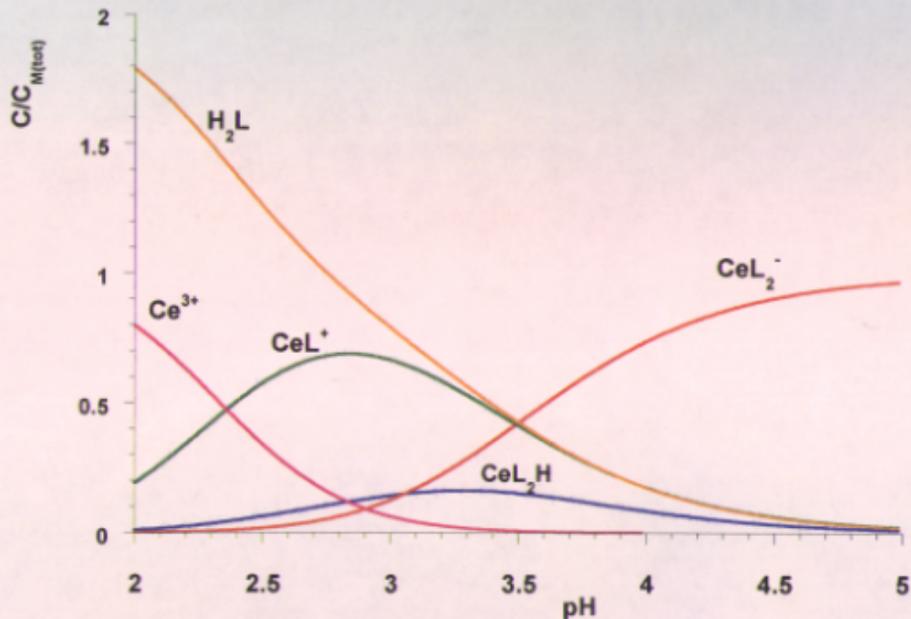
Stability Constants of Ce(III) Complexes with Me-3,2-HOPO Ligands

Ligand	$\log\beta_{110}$	$\log\beta_{111}$	$\log\beta_{112}$	$\log\beta_{120}$	$\log\beta_{121}$	$\log\beta_{130}$	$\log\beta_{140}$
Me-HOPO	6.07			11.01		14.56	
PR-HOPO				11.12		15.78	19.70
5LI-HOPO				21.60	24.94		
5LIO-HOPO	11.36			20.89	24.11		
TREN-HOPO	17.41		24.77				
H(2,2)-HOPO	20.35	26.66	30.27				

Correlation between Stability Constants of Ce(III) Complexes with Bidentate and Tetradentate HOPO Ligands and the Number of HOPO Groups in Them



Species Distribution for Ce(III) with 5LI-O-3,2-Me-HOPO (1:2)



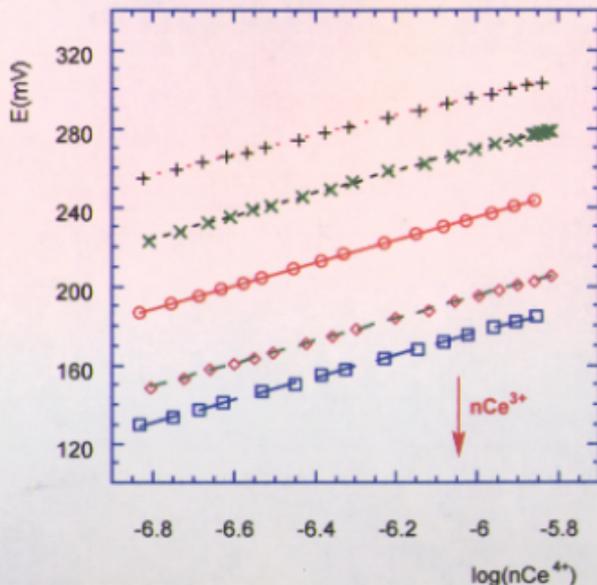
Potentiometric Data for the Ce/5LI-O-3,2-Me-HOPO (1:2) System

$$E = E^{\circ} - RT/nF \ln([Red]/[Ox])$$

$$E = E^{\circ} - 59.1/n \log [Ce(III)] + 59.1/n \log [Ce(IV)]$$

$$E = E^{\circ} - 59.1/n \log nCe(III) + 59.1/n \log nCe(IV)$$

Each line corresponds to a different amount of Ce(III)



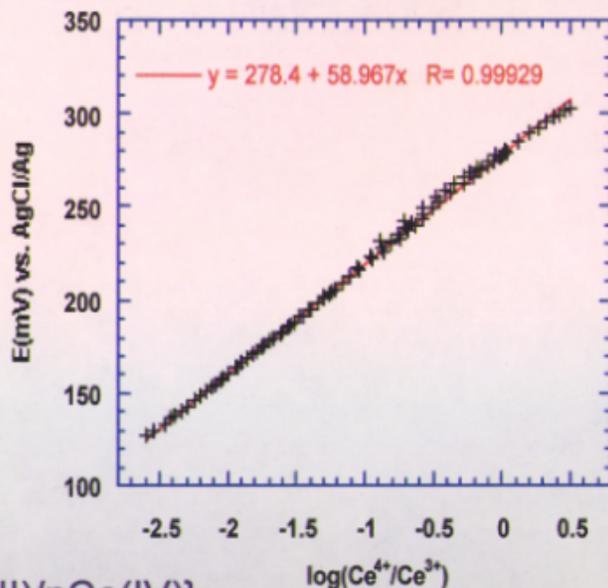
Nernstian Plot for the Ce/5LI-O-3,2-Me-HOPO (1:2) System

$n = 1$

$E^\circ = +81 \text{ mV vs. NHE}$

For the $\text{Ce}^{4+}/\text{Ce}^{3+}$
couple,

$E^\circ = +1700 \text{ mV vs. NHE!}$



$$E = E^\circ - 59.1/n \log \{n\text{Ce(III)}/n\text{Ce(IV)}\}$$

Osteryoung Square Wave Voltammetry Data for Ce(IV)/Ce(III) Couples of HOPO Complexes

Ligand	M:L Ratio	E° vs. AgCl/Ag	E° vs. Ce(IV)/Ce(III)	$\Delta \log \beta^*$
PR-HOPO	1:4	+248	-1649	27.87
5LI-HOPO	1:2	+308	-1589	26.86
5LIO-HOPO	1:2	+276	-1621	27.40
TREN-HOPO	1:2	+236	-1661	28.08
H(2,2)-HOPO	1:1	+312	-1585	26.79
Average		+276	-1621	27.40

* $\Delta \log \beta$ give *the increments in orders of magnitude* for the stability constant values of the Ce(IV) complexes versus the corresponding Ce(III) complexes.

All data (in mV) were obtained on a glassy carbon electrode in 0.1 M KCl.

Practical Evaluation of a Ligand at Different pH

- Need a value that reflects the proton competition for the ligand that exists in aqueous solution
- Use pM values calculated for different pH

$$\text{pM} = -\log[\text{M}]$$

$$[\text{L}]_{\text{total}} = 10^{-5} \text{ mol/l}, [\text{M}]_{\text{total}} = 10^{-6} \text{ mol/l}$$

pH

7.00

2.00

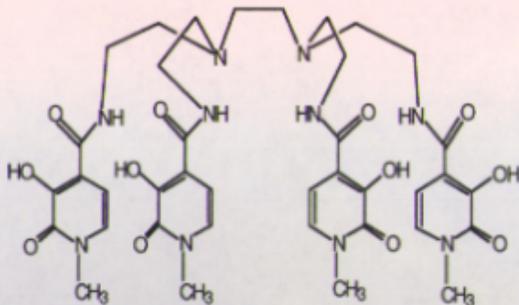
0.00

pCe

46.0

24.3

12.5



Conclusions

- The flexible coordination geometry in HOPO complexes of Ce(IV) implies **no rigorous steric requirements towards the ligand**
- The similar stability constants of coordinatively saturated HOPO complexes of Ce(III) and the similar formal potentials of the corresponding Ce(IV)/Ce(III) pairs suggest that **stability is primarily dependent on the number of HOPO groups bound to the metal**
- The large values of pM calculated for Ce(IV) at low pH show that **HOPO ligands are perfectly suitable as extractants from acidic waste**