f-Element Ion Chelation in Highly Basic Media

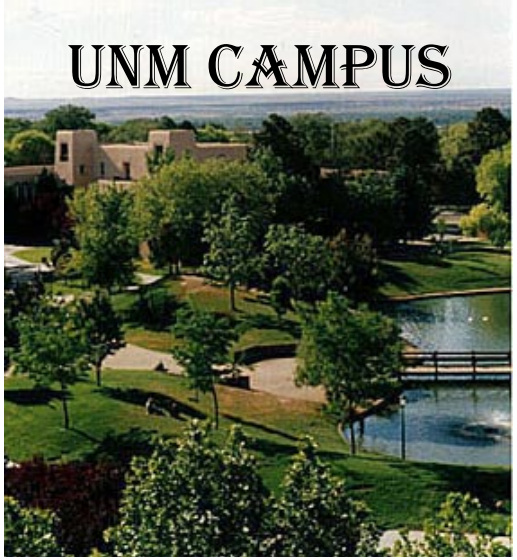
Project P.I.: R. T. Paine

Project Coworkers: X. Gan, G. Claycomb, N. Karsten, E.N. Duesler and J. Fox

Department of Chemistry,
University of New Mexico,
Albuquerque, NM USA

Project Number: 54595 NM

Focus Areas: High Level Waste
Decontam./Decomm.



I. Introduction

A. Background

- DOE has temporarily stored large volumes of complex, radioactive waste materials in tanks at the Hanford facility.
- Much of the waste has been stored in basic media in order to reduce tank corrosion.
- The poorly characterized liquid and solid waste components must now be converted to a geologically stable, solid waste form for long term storage.
- Considerable cost savings could be realized by separation of the most highly radioactive fission products from less hazardous components.

B. General Problems

Most well developed separations chemistry for fission product f-element ions operates on simple aquo ions, $M(H_2O)_x^{n+}$ or $MO_2(H_2O)_x^{2+}$, present in aqueous acid media.

- The composition and chemistry of f-element ion species in basic media differs greatly from those of acidic solution species.
- f-Element ions tend to hydrolyze at near neutral pHs $\longrightarrow$ poorly characterized poly-metallic oxo-hydroxo species.
- Fundamental coordination chemistry of oxo-hydroxo species is poorly developed.
- Hence, fundamental knowledge to support development of appropriate basic media separations schemes is lacking.

II. Project Goals

Enlarge the knowledge base on the fundamental chemistry of f-element ions in basic solutions through:

- Study of the hydrolysis and speciation behavior of fission product ion mimics, e.g. Ln^{3+}, Sr^{2+}, as function of pH and counter ions.
- Study the formation of hydrolysis oligomers and the kinetics of sol $\longrightarrow$ gel $\longrightarrow$ ppt. transformation.
- Study the coordination and dissolution behavior of oligomeric oxo-hydroxo metallate species as a function of pH and counter ion.

- Develop new classes of ion specific chelators stable toward alkaline solutions.
- Study ion specific chelators as oxo-hydroxo metallate dissolution modifiers.
- Utilize the new data to devise new chelator/basic media waste separations and decontamination protocols.

III. Experimental

A. Solubility/Speciation of Ions in Basic Media

Objectives

- Characterize pH of hydrolysis on-set as a function of M^{n+} and counter ion.

  * *methodology: pH titrations and light scattering.*

- Characterize oxo-hydroxo metallate oligomer growth kinetics.

  * *methodology: light scattering*

- Characterize oxo-hydroxo metallate species solubility.

  * *methodology: ICP-ES*

- Characterize speciation of soluble fractions.

  ** methodology: ICP-MS and ^{89}Y NMR*

- Characterize speciation of insoluble fractions.

  ** methodology: x-ray crystallography ^{89}Y CP-MAS NMR*

A. Solubility/Speciation of Ions in Basic Media

Summary of Results

1. Hydrolysis on-set pH for $M(NO_3)_x$ Salts

Compound (0.01M)	pH
$Sr(NO_3)_2$	10.0
$Y(NO_3)_3$	6.5
$La(NO_3)_3$	7.6
$Nd(NO_3)_3$	6.8 - 7.0
$Er(NO_3)_3$	6.5

Conclusion: general agreement with literature

The University of New Mexico

2. Hydrolysis on-set pH for $M(NO_3)_x$ Salts

Ionic Strength Shift

$M(NO_3)_3$ = 0.01M $La(NO_3)_3$

Salt conc	KNO_3	pH	KCl
0.0M	7.6		7.6
0.1M	7.4		6.8
0.5M	7.2		6.7
1.0M	6.7		6.5
3.0M	6.5		6.3

Conclusion: As expected, increasing ionic strength shifts hydrolysis on-set pH to lower values.

Similar results with other M^{3+} ions

The University of New Mexico

3. Hydrolysis on-set pH for $M(NO_3)_x$ Salts Coordinating Counter Ion Shift

$M(NO_3)_3$ =0.0lM $La(NO_3)_3$

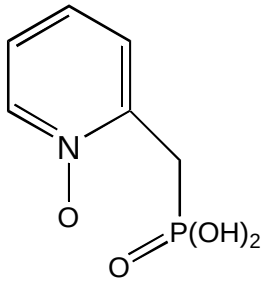
Compound	M/L ratio	pH value	Observation
Acetic acid	1:3	7.6	Hydrolysis
	1:7	7.8	Hydrolysis
Acetylacetone	1:3	7.7	Solid Complex Formed
Benzoic Acid	1:3	5.0	Solid Complex Formed
Citric acid	1:3	>14.0	No Hydrolysis
Malonic acid	1:3	4.0	Solid Complex Formed
Oxalic acid	1:3	2.0	Solid Complex Formed
	1:6	2.0	Solid Complex Formed
Phthalic acid	1:3	5.0	Solid Complex Formed
Salicylic acid	1:3	6.3	Solid Complex Formed
EDTA	1:1	14.0	No hydrolysis

Conclusions: Acetic acid/acetate shows no shift in hydrolysis pH while citric acid/citrate and EDTA/Na_2EDTA show large shifts. The other acids form solid ppts.

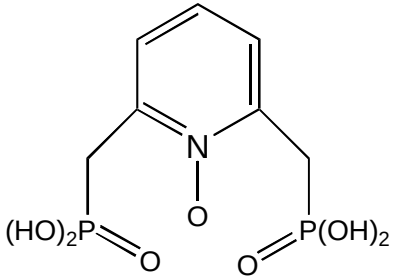
The University of New Mexico

4. Hydrolysis on-set pH for $M(NO_3)_x$ Salts Coordinating Phosphonic Acid Shifts

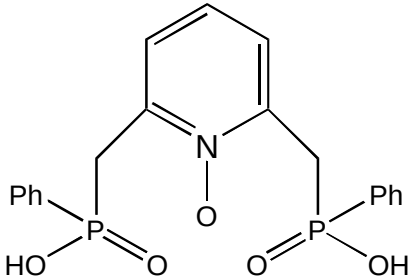
New Phosphonic Acids



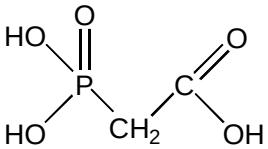
1



2



3



4

$M(NO_3)_3$ = 0.01M $La(NO_3)_3$

M/L Ratio/pH values for hydrolysis

Compound	1:1	1:2	1:3	1:4	Observation
1	8.2	8.6-8.9	9.4	9.4	No hydrolysis
2	13.4	13.7			No hydrolysis
3	2.0				Solid complex forms
4	2.0-3.0	2.0			Solid complex forms

Conclusions: **1** shifts the on-set hydrolysis pH and forms a soluble complex. Above pH 9.5 the complex undergoes hydrolysis. **2** strongly shifts the on-set hydrolysis pH to a range similar to EDTA. **3** and **4** do not shift the on-set pH.

5. Speciation Study on Systems Containing Ligand **2** and Nd^{3+}, Eu^{3+}, Th^{4+} and UO_2^{2+}

Summary of Potentiometric Titrations

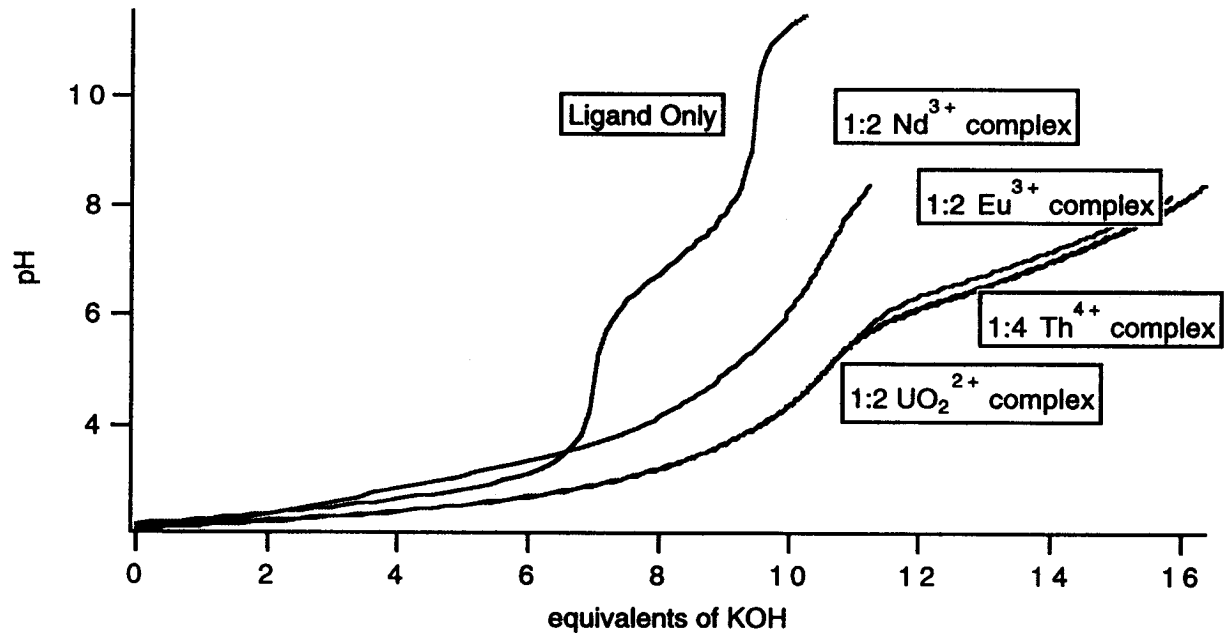


Figure 1. Plot of pH vs. equivalents of KOH for **2** and it's complexes.

The University of New Mexico

Summary of Speciation Behavior

$M=Nd(NO_3)_3$ 2.5×10^{-3} M

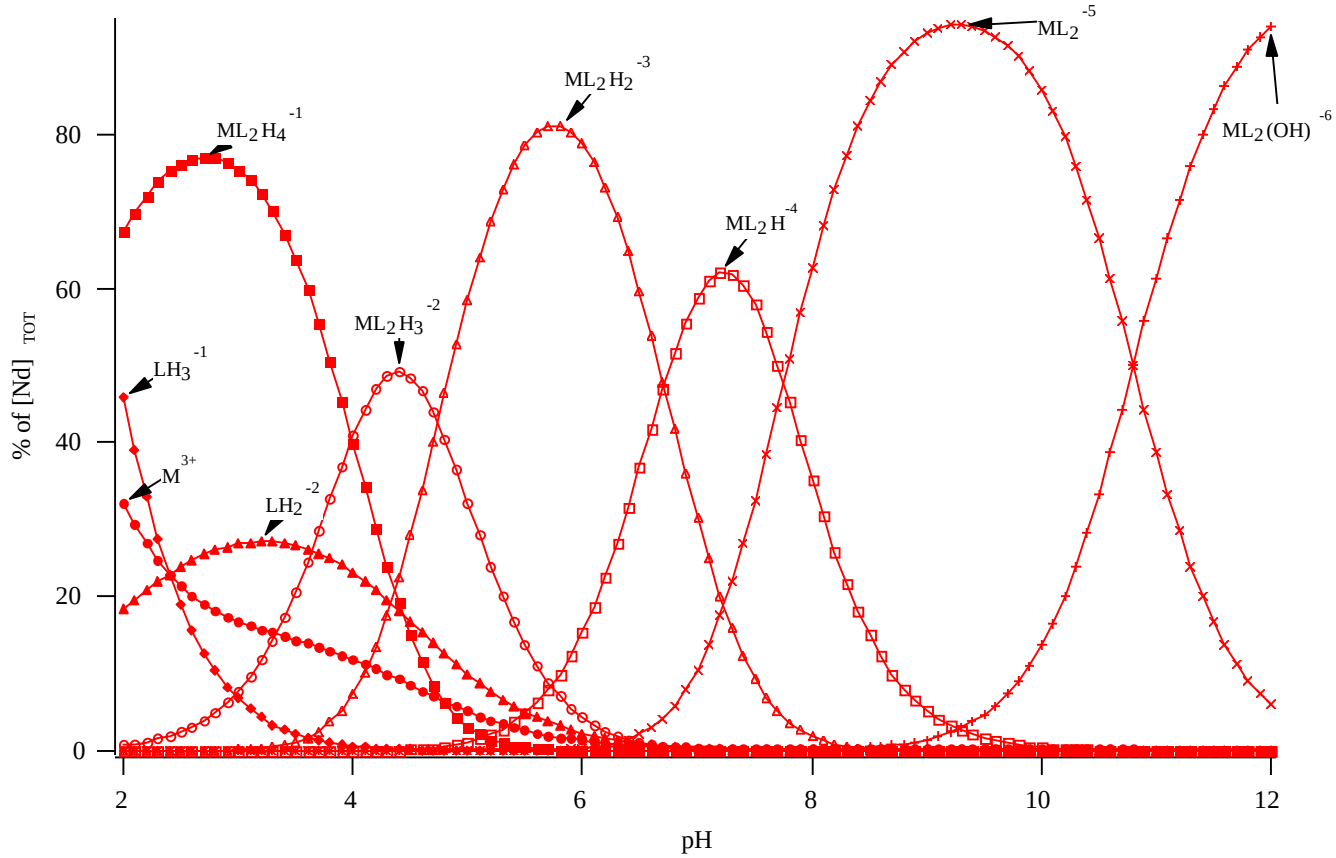


Figure 2. Speciation of Ligand **2** with Nd(III) as a function of pH.

The University of New Mexico

Conclusion: Ligand **2** forms a large array of soluble complexes with Nd^{3+}, Eu^{3+}, Th^{4+}, UO_2^{2+}, and each is soluble up to at least pH12. Speciation behavior of Nd(III) has been modeled as shown in Figure 2. Hydroxo species may form only above pH 9. Attempts to isolate specific complexes are in progress.

The University of New Mexico

B. Oxo-Hydroxo Metallate Species Growth Kinetics

Objective

A semi-quantitative picture of the kinetics of lanthanide ion hydrolysis is needed in order to understand the oligomerization processes and the influence coordinating ligands have on oligomerization.

Summary of Results

Solutions of $La(NO_3)_3$ (0.01M) were combined with KOH solution (2.5-3.5 ml, 0.01M) and the kinetics of oligomer growth followed by light scattering.

Selected data are shown in Figure 3.

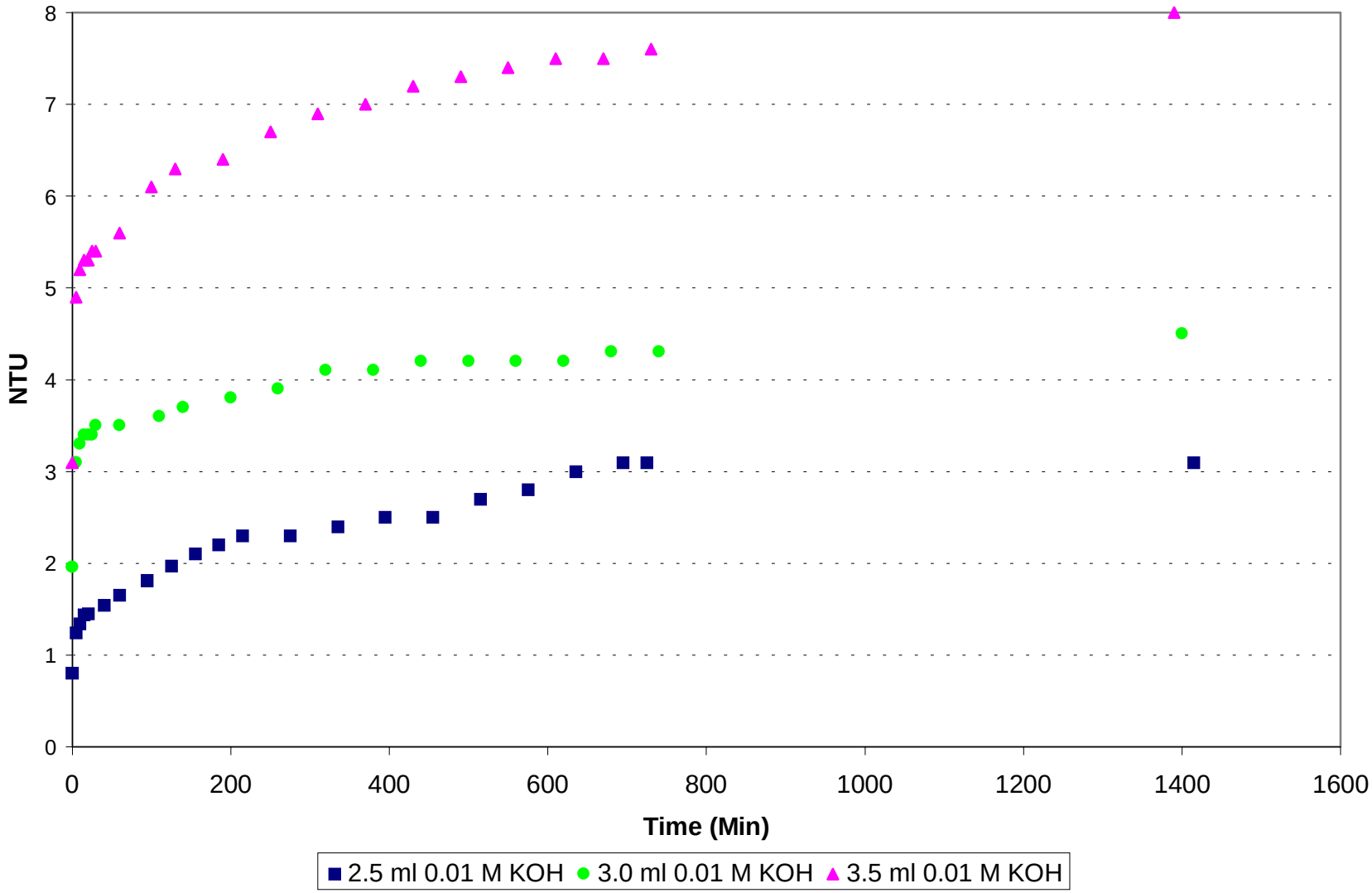


Figure 3. Light scattering intensity vs. time for a solution of $La(NO_3)_3$ (0.1M) with added KOH

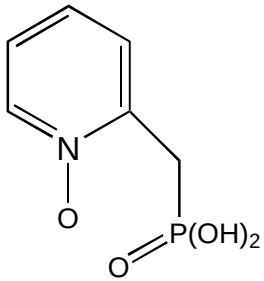
The University of New Mexico

Conclusion: The oligomerization process contains an initial fast growth process and a second slow growth process independent of the amount of KOH used. The additional KOH appears to only result in larger particle growth, and some what faster initial hydrolysis.

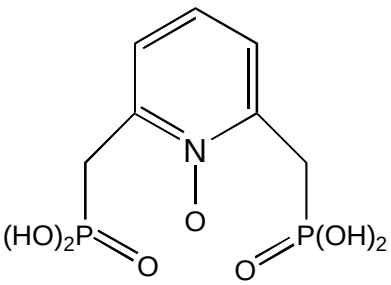
C. Characterization of Complexes

Objective

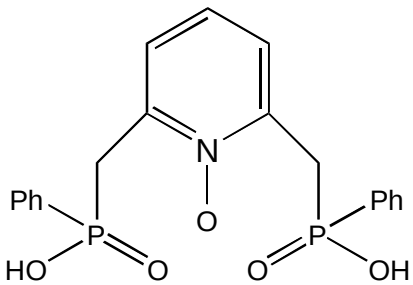
New phosphonic acid chelators, e.g., **1- 4**, form stable coordination complexes with $Ln(NO_3)_3$ salts and they also dissolve and coordinate with $Ln(OH)_3$ and complex oxo-hydroxo species. The structures of these complexes are of interest since they provide clues on how to modify the ligands to achieve improved binding behavior.. Hence, the crystal structures of various species are being explored.



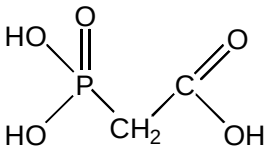
1



2



3



4

The University of New Mexico

Formation of Complex **5**

$$Er(OH)_3 + 4\,\mathbf{1} \xrightarrow{H_2O} \text{ppt.} \xrightarrow[\text{2. evap}]{\text{1. }\triangle} Er(\mathbf{1}^-)_3\,(\mathbf{1}) \bullet 4H_2O$$

A view of the structure is shown in Figure 4 and the coordination polyhedron is shown in Figure 5.

Description:

The inner coordination sphere contains four ligand units each bonded in a bidentate fashion to the central Er(III) ion. One ligand **1** retains both acidic protons on the phosphonic acid. Three ligands have each lost one H^+ and each ligand carries a negative charge. The inner coordination sphere is a square antiprism.

The University of New Mexico

Conclusion: Crystallography reveals the nature of the interaction between phosphonic acid ligands and metals. This and additional structural studies will aid in the design of new, more efficient chelators.

IV. Future Activities

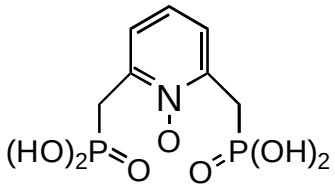
Summary

- Results described above provide initial insight into the complex coordination chemistry displayed by f-element ions in basic media.
- Results described above indicate that some phosphonic acid ligands are good chelators for Ln^{3+} ions at basic pH.
- These observations suggest that additional studies will shed light on the formation of f-element/phosphonic acid complexes.

Further Work

- Study the formation of $Ln(OH)_3$ and $Ln_2(CO_3)_3$ species in greater detail by use of light scattering techniques.
- Study the speciation of phosphonic acid complexes in more detail by NMR and mass spectrometry.
- Study the molecular structures of isolated coordination complexes by x-ray diffraction methods.
- Undertake additional phosphonic acid ligand development in search of improved dissolution agents.

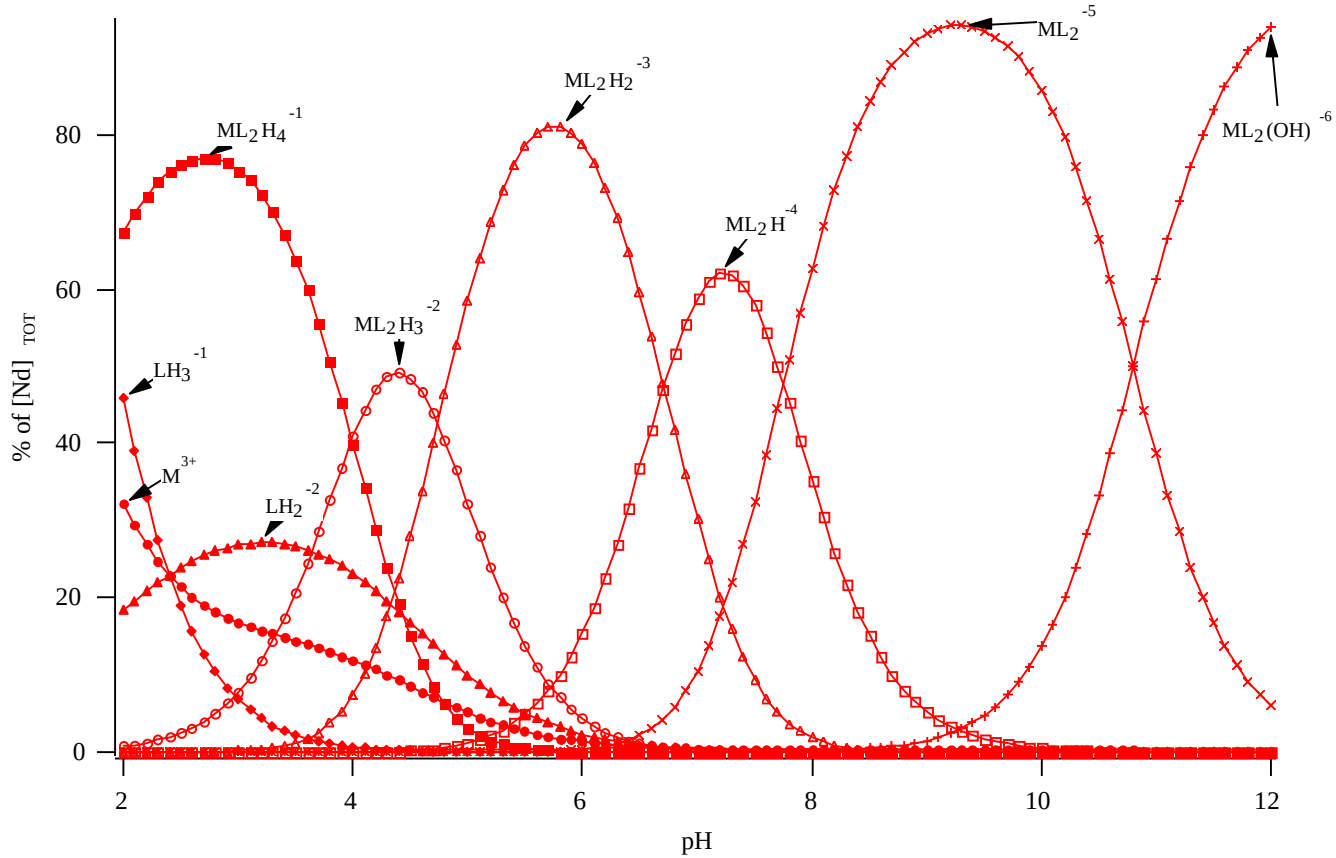
Phosphonic Acid



Binds Ln^{3+} in Basic Solution

Dissolves $Ln(OH)_3$ and $Ln_2(CO)_3$

$M=Nd(NO_3)_3$ 2.5×10^{-3} M



The University of New Mexico