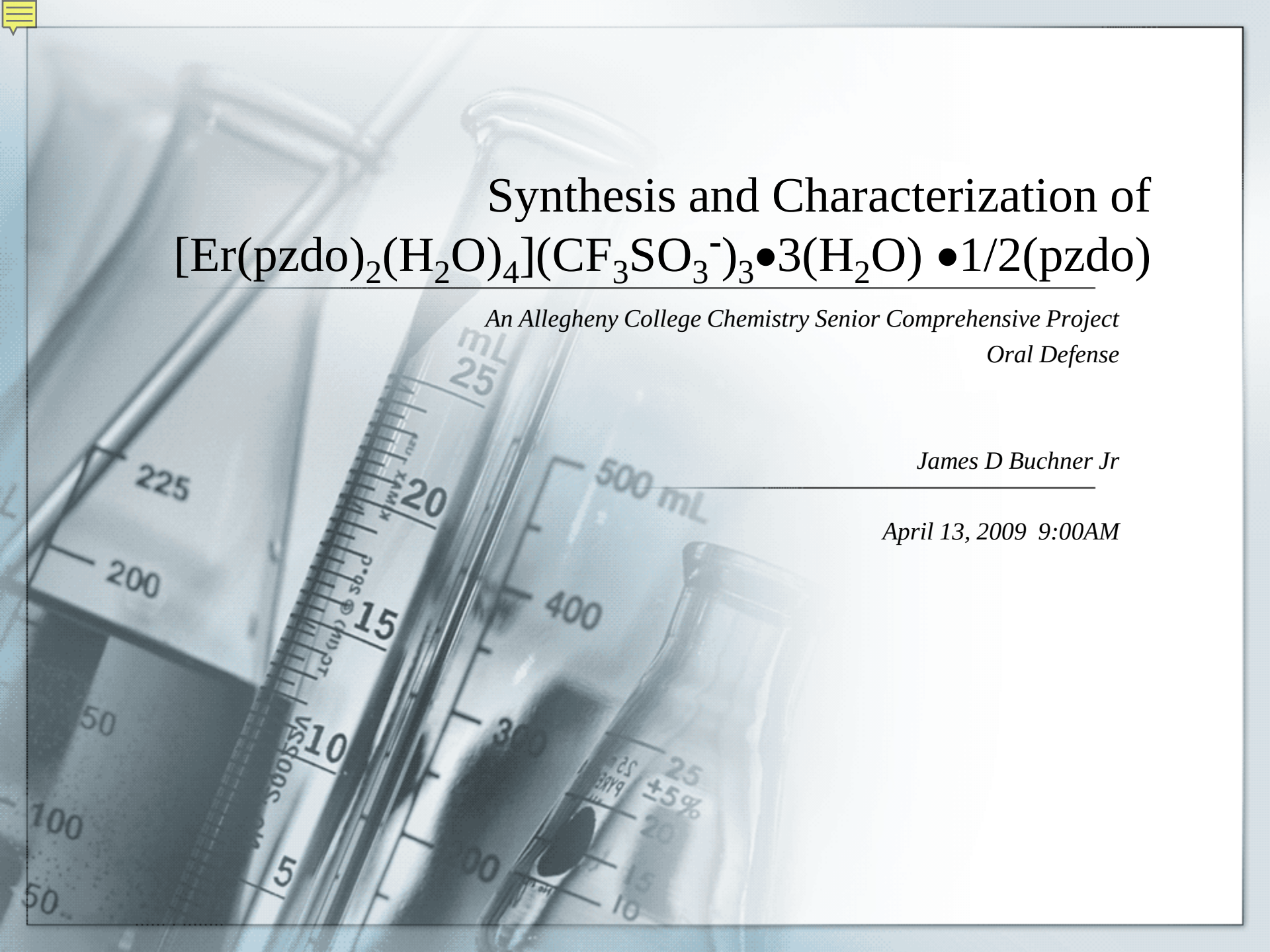


Synthesis and Characterization of $[Er(pzdo)_2(H_2O)_4](CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$

An Allegheny College Chemistry Senior Comprehensive Project Oral Defense

James D Buchner Jr

April 13, 2009 9:00AM

Abstract

- The objective of this research was to synthesize a lanthanide coordination polymer in order to study the intermolecular bonding forces.
- The Lewis acid and basicity of the lanthanide metal Er^{+3} and a selected ligand, pyrazine-N,N'-dioxide were studied to project the nature of coordinate covalent bonding.
- The $[Er(pzdo)_2(H_2O)_4]\ (CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$ coordination network was synthesized.
- X-Ray Diffraction was used to study the nature of the crystal structure its intermolecular forces.

Coordination Networks

- Self Assembly Synthesis
  - Ordered structured product obtained from an unordered mixture of building blocks
  - Coordinate-covalent bonding of ligands
  - Weaker interactions play important roles in the 3D self assembly process to build up network

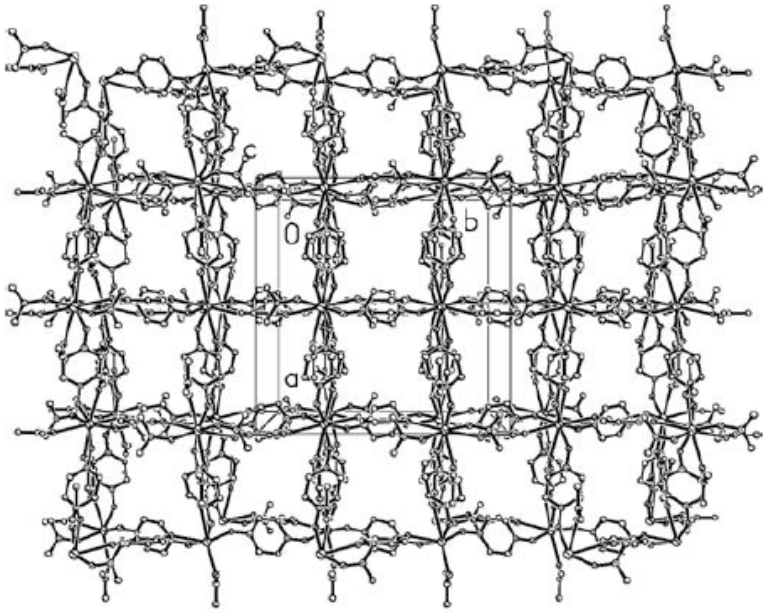


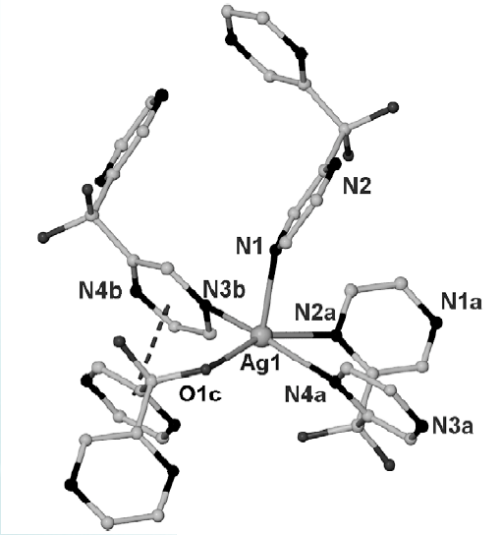
Figure 1: Three Dimensional open-framework of a coordination network; $Pr(pzdo)_4(ClO_4)_3$

Picture courtesy of:

Sun, H.L, Gao, S. *Microporous and Mesoporous.* **2004**, 73(2), 89-95. Pp. 93

Coordination Networks (2)

- Metal “node” Chemistry
  - d-block metals have smaller radii and limited coordination number
  - f-block metals have larger radii and higher coordination numbers



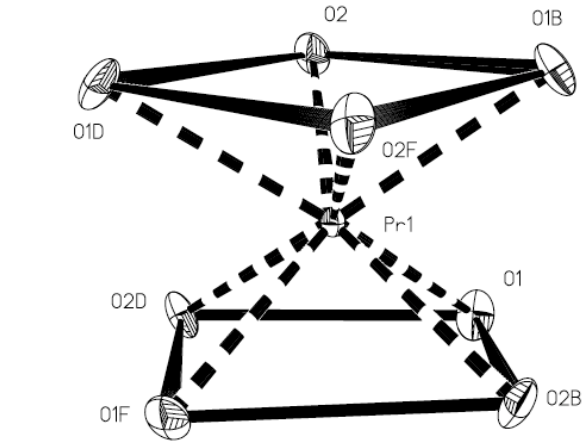


Figure 2 (above): Shows a coordination environment for a single Silver atom in a coordination network using a d-block metal center.

Courtesy of:

Wan, C-Q., Mak, C.W. *Inorg. Chimica Acta*. **2008**, (361)5, 1496-1502. Pp. 1500.

Figure 3 (below): Shows a single Praseodymium metal center coordinated to eight oxygen atoms in a square anti-prism geometry.

Courtesy of:

Sun, H.L, Gao, S. *Microporous and Mesoporous.* **2004**, 73(2), 89-95. Pp. 93

Coordination Networks (3)

- Bi-functional ligand “spacers”
  - Bi-functional ligands promote 3D structure; each ligand can bind with two or more metal ion nodes
  - The distance between the nucleophilic sites of the ligands regulate the cavity size

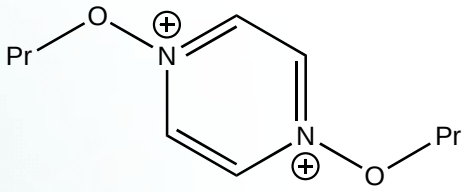


Figure 4: A ChemDraw® representation of pyrazine-N,N’-dioxide (pzdo) acting as a bridging ligand between two Praseodymium metal centers.

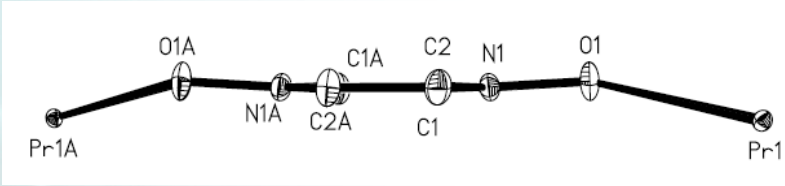


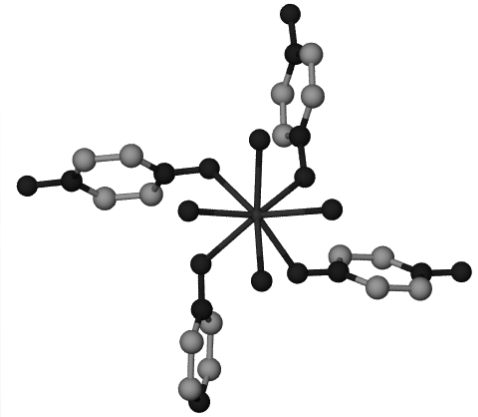
Figure 5: A stick representation of pzdo bridging two metal centers, this is a representation of the same systems involving Pr that we have discussed in the previous two slides.

Courtesy of:

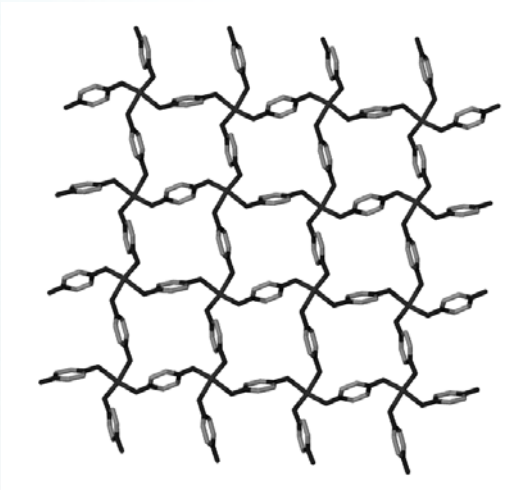
Sun, H.L, Gao, S. *Microporous and Mesoporous.* **2004**, 73(2), 89-95. Pp. 93

Previous Research

- The coordination geometry of a single Praseodymium metal center, coordinated to four bidentate ligands and four waters.



- A network of interconnected Praseodymium metal centers revealing a porous 2-D sheet. The empirical formula was derived by XRD to be: $[Pr(pzdo)_2(H_2O)_4]\ (CF_3SO_3^-)_3 \cdot 3(H_2O)$



Preference of Ligand

- Pyrazine-N,N'-dioxide
- Pearson's Hard Soft Acid Base Theory

$$n_A = \frac{1}{2}(I_A - A_A)$$

- Aromatic rings are beneficial due to their ability to ∏-∏ stack and form 3-D networks once 2-D sheets were formed.

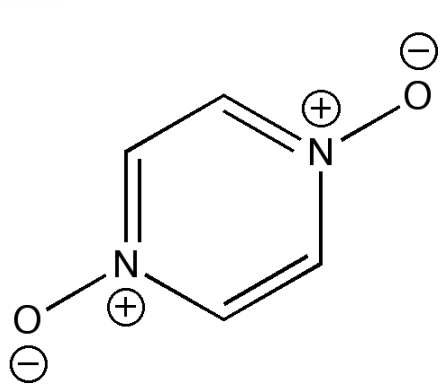
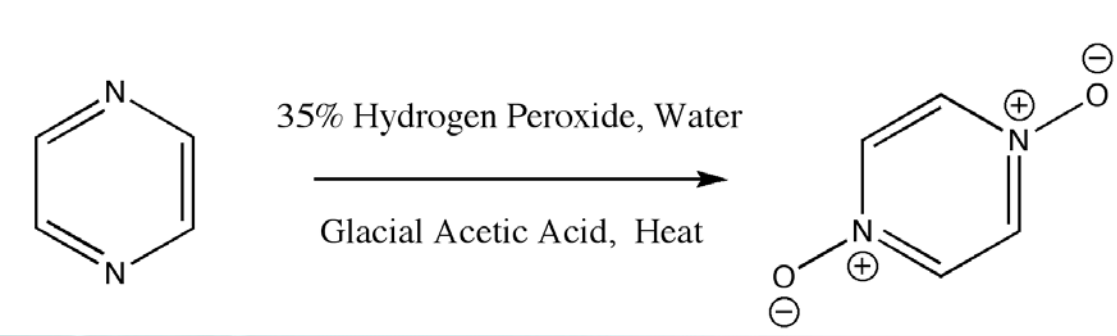


Figure: A ChemDraw® structure of pyrazine-N,N'-dioxide. The partial charges on both the oxygen and nitrogen atoms make this a very favorable bridging ligand for coordination networks.

Synthesis of Materials

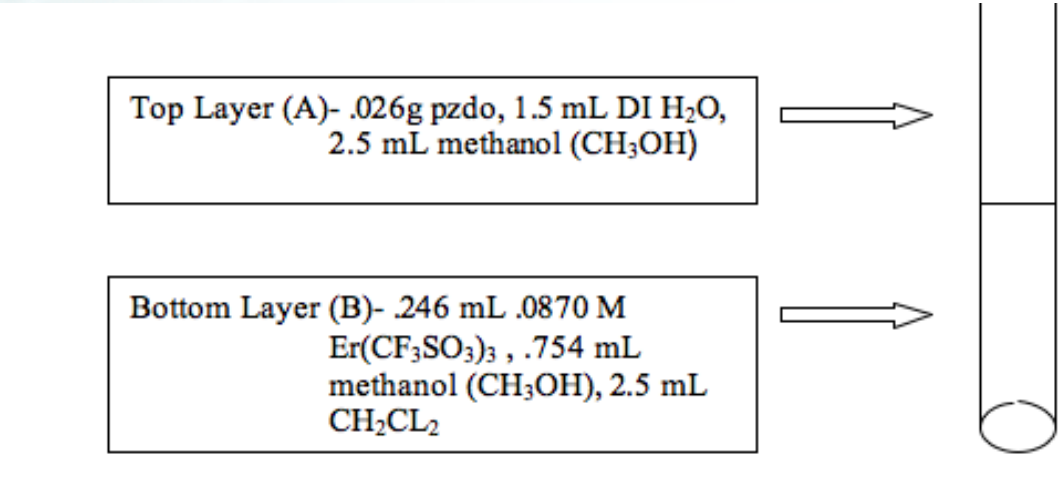


- Synthesis of prazine-N,N'-dioxide ligand

- 4.343 g of pyrazine was combined with 40.0 mL of Acetic Acid and 20 mL 35% Hydrogen Peroxide, this mixture was heated and stirred on a hot plate at 75 C, after three hours another 15.1 mL portion of 35% Hydrogen Peroxide was added

- After 12 hours in the flask, 20 mL of Water was added and then distilled at 100 C. The yellow oil derived was combined with 150mL of actone and a white flaky power precipitated out of solution.

Synthesis of Coordination Polymer



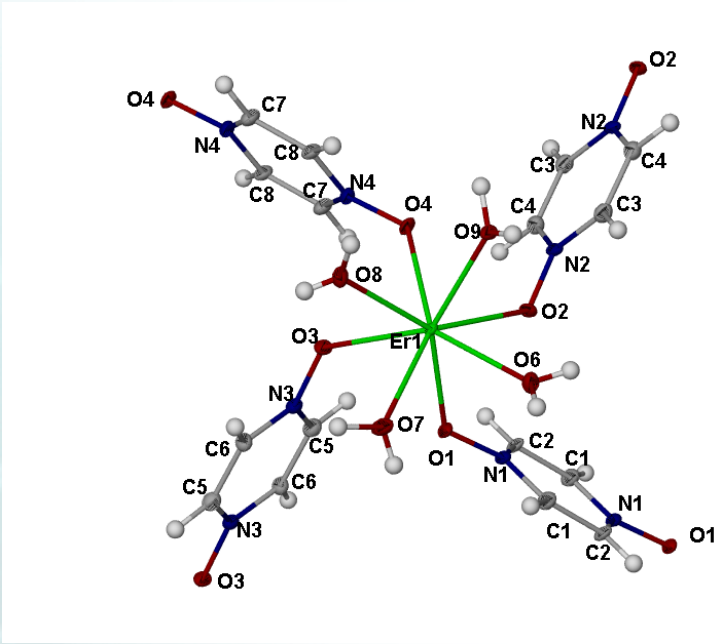
- A technique called layering was used to form;

$[Er(pzdo)_2(H_2O)_4](CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$

Layering allows for slow dissipation of the two mixtures, creating a gradual crystallization process.

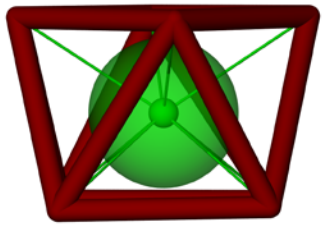
$[Er(pzdo)_2(H_2O)_4]\ (CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$

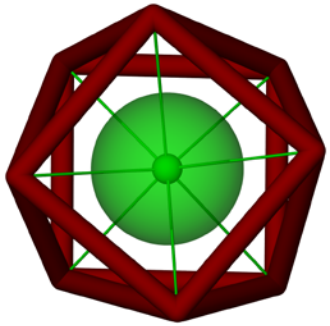
- The Erbium metal center is coordinated to four pzdo molecules.
- All of the coordinated pzdo must be bridged between two metal centers (bidentate in nature)
- Empirical formula derived from X-Ray Diffraction analysis.



Coordination Environment of Er

- These two figures represent the coordination environment of the metal center, Erbium.
- Eight substituents (Oxygen's from coordinated waters and pzdos) surround each Er center, and are arranged as such to form square anti-prism geometry.
- Coordination geometry is offset by approximately 45 degrees, resulting in a lower free energy as opposed to a square prism geometry.

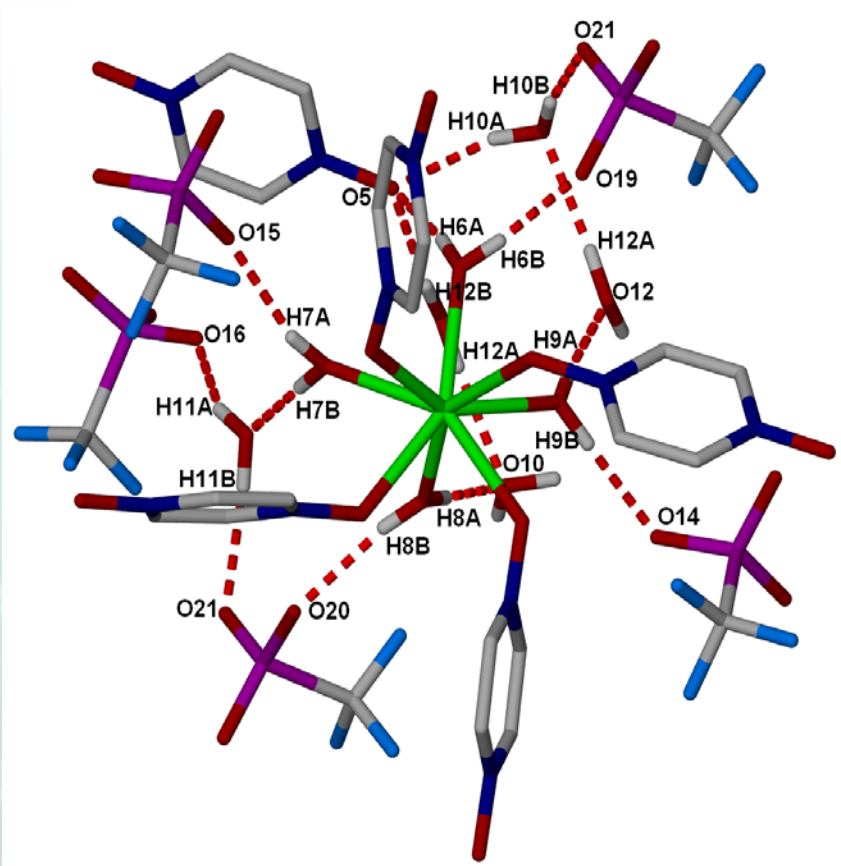




Expanded Coordination Environment

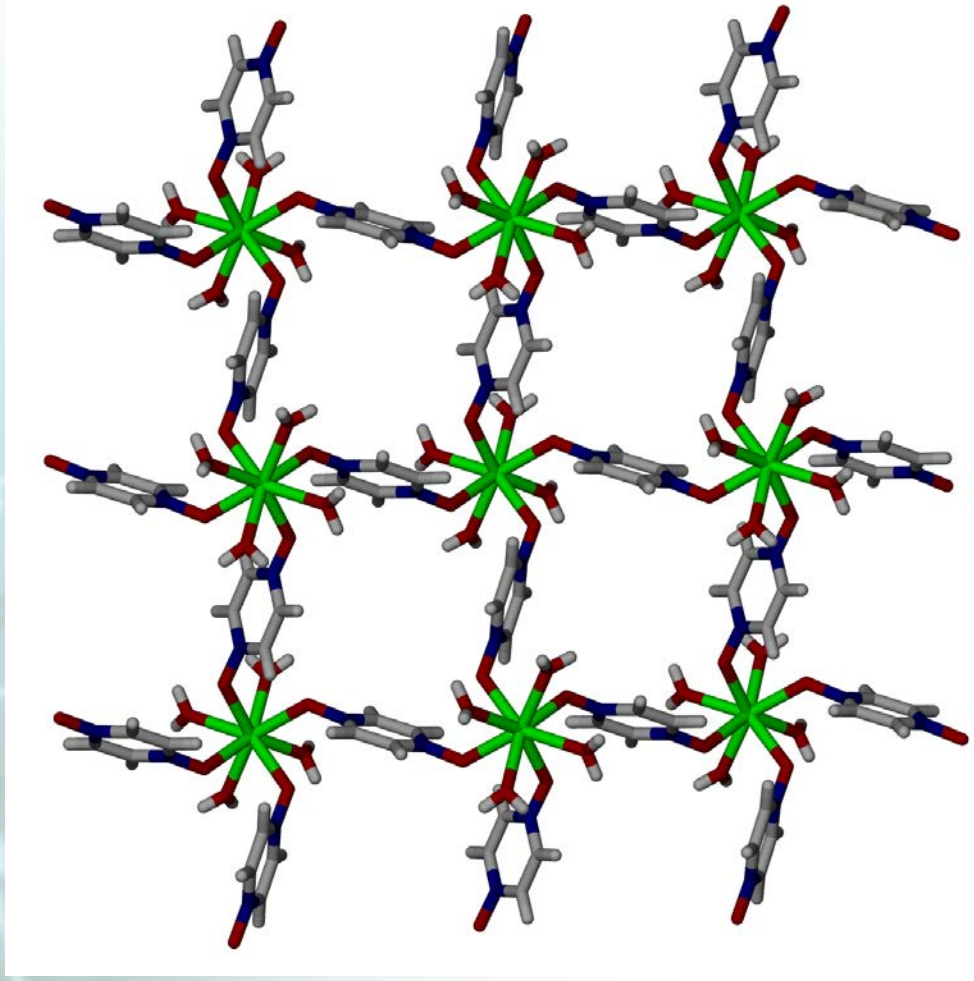
- This figure, unlike the first model of $[Er(pzdo)_2(H_2O)_4]\ (CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$ shows the Hydrogen bonding present around the central Er metal center.

- Nine water molecules in total are shown in this figure. Four water molecules are coordinated directly to Er, five are loosely bound. Four of the H-bound waters were shared with neighboring metal centers.



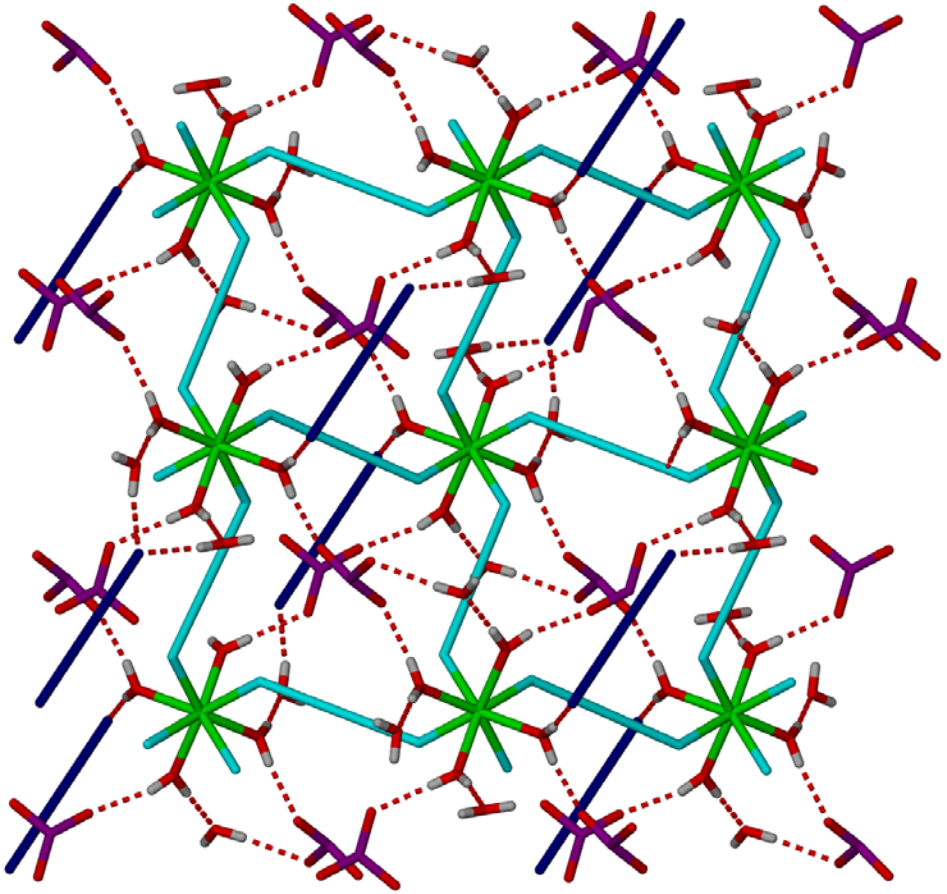
Two Dimensional Sheet

- This figure is an image taken as looking down the c-axis
- The porous channels are revealed when the H-bound molecules are omitted.

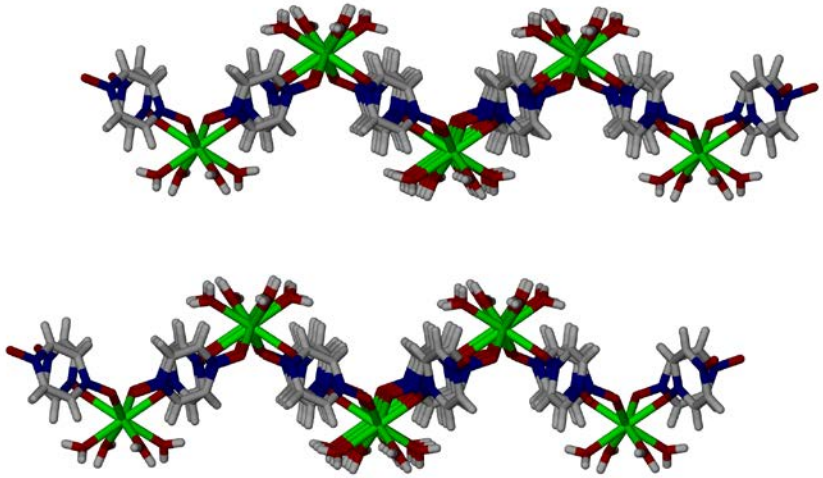


Two Dimensional Sheet (2)

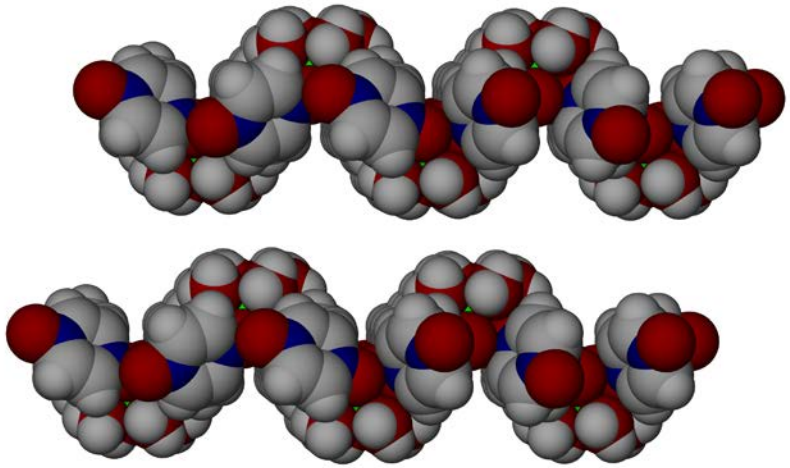
- Similar view down the c-axis, however the ligand pzdo was converted to an aqua colored bar to show the H-bonding in the network more clearly.
- The H-bound pzdo ligands are shown in the dark blue bars.



Three-Dimensional Layers



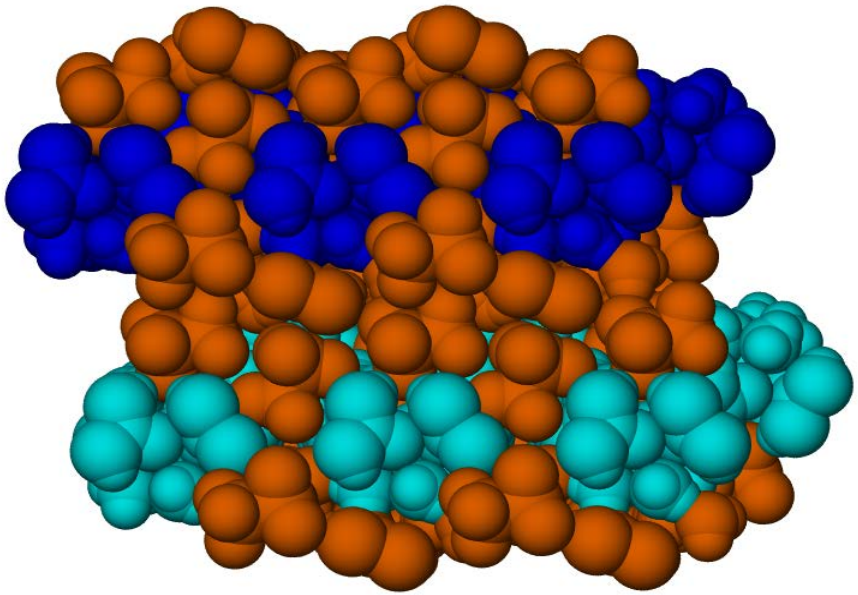
(Left): Wireframe representation of two layers and their space between each other. Erbium metals are shown in green and can be seen at the inflection points of the structure.



(Right): A bubble (or space fill) representation of two layers of $[Er(pzdo)_2(H_2O)_4]\,(CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$. Similar to before, the H-bonded constituents are omitted to show the space between the layers.

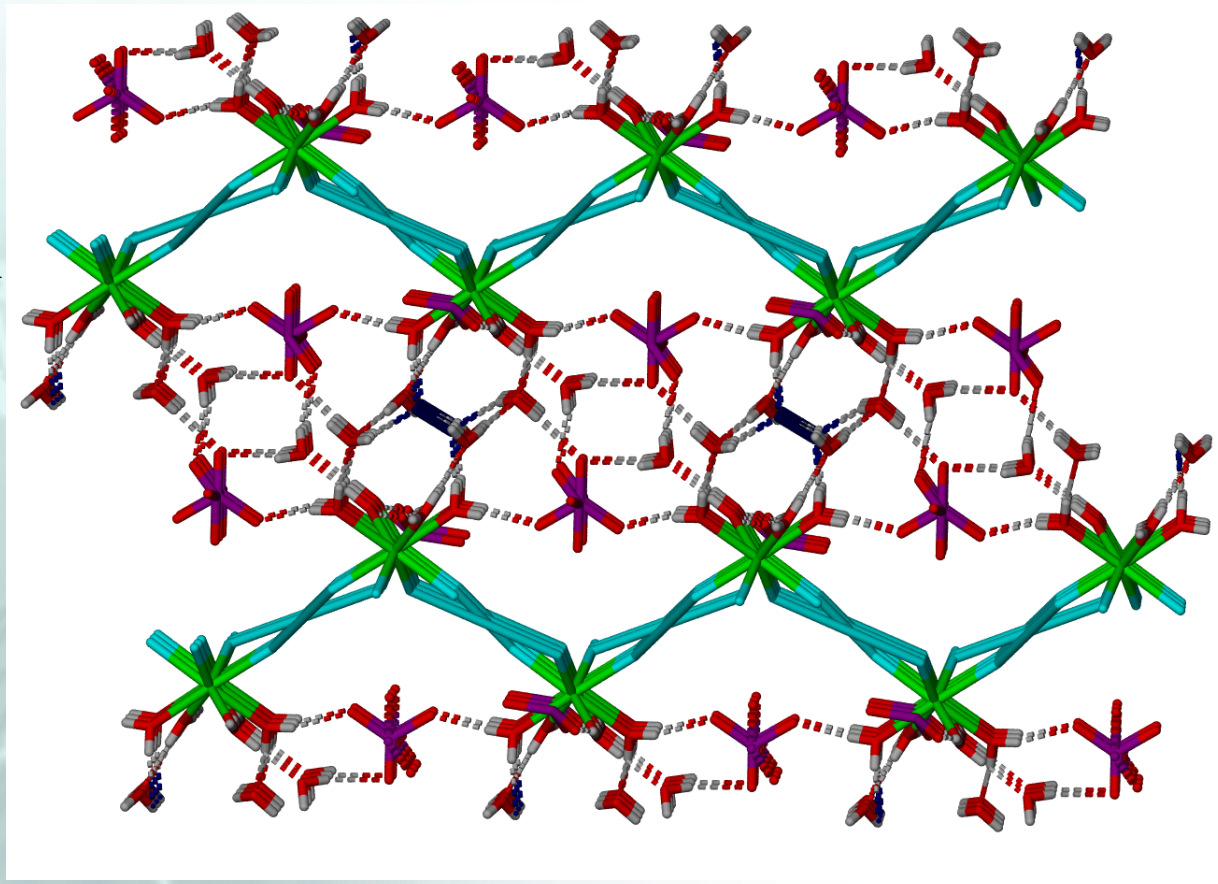
Three-Dimensional Layers (2)

- The same two layers shown in the previous slide can be seen here colored blue and aqua. All of the orange molecules are those that are H-bonded and not within the primary coordination sphere of the Er metals.



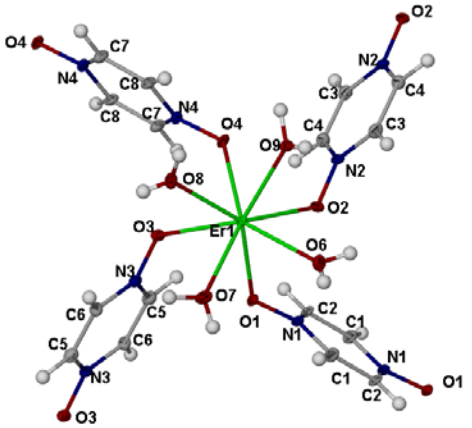
Hydrogen Bonding between Layers

- This figure shows a wireframe representation of the H-bonding between two layers of $[Er(pzdo)_2(H_2O)_4](CF_3SO_3^-)_3 \bullet 3(H_2O) \bullet 1/2(pzdo)$



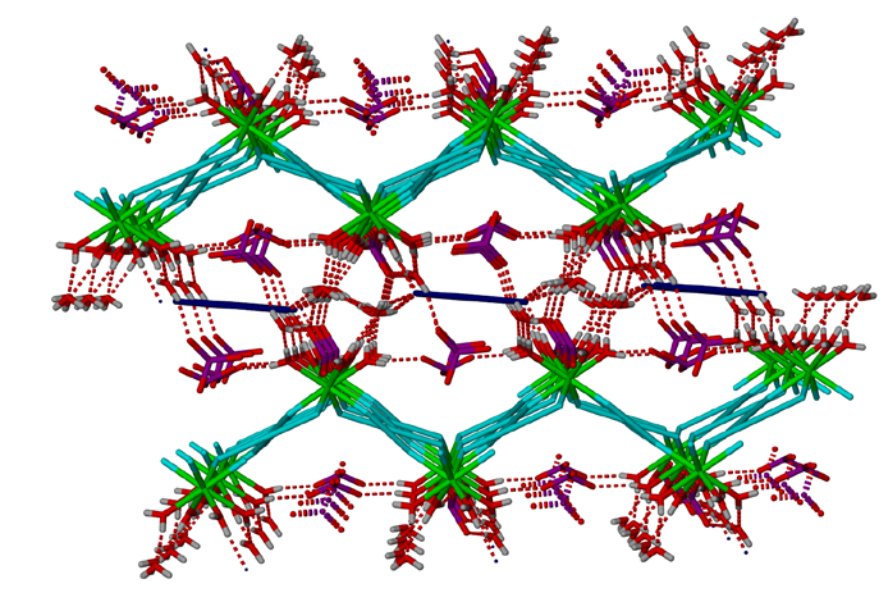
Conclusions

- A Lanthanide coordination polymer was successfully synthesized by the “layering” method and then characterized by X-Ray Diffraction.
- The intermolecular forces of this network were analyzed and studied. Multiple factors (concentration, technique, and total volume) were varied, however only this specific reaction yielded a successful result for the Er metal in my experiment.
- The time for crystallization was extremely long, and other methods should be studied in an attempt to shorten this time span.



Future Work

- Thermogravimetric analysis could be used to test this networks stability at high temperatures, and to reveal additional insight into the non-coordinated water molecules.
- Elemental analysis also could be useful in verifying the empirical formula and overall atomic composition of the network.
- Reactions to test potential applications of these networks could lead to some interesting research. A good start would be to design and run a reaction similar to the one I proposed at the end of last semester.



Acknowledgments

- Many thanks to Dr. Knaust and Dr. Zeller for their help with the X-Ray Diffraction analysis and structure refinement.
- Thank you to Bob, without your help on providing massive amounts of acetone and other chemicals to me over the years I would have never gotten anything made.
- Thank you to my lab group, going through this with all of you made it a somewhat enjoyable process!

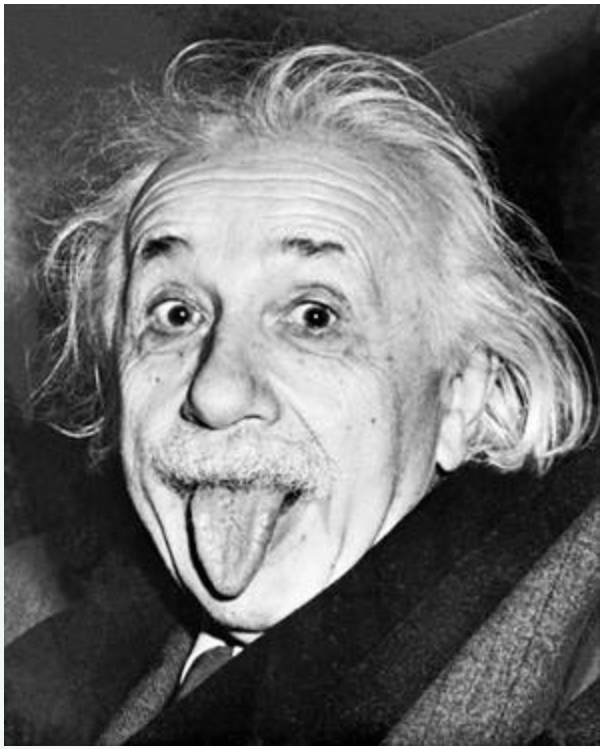


Table of Crystal Data

Identification code	07jb009m
Empirical formula	C13 H24 Er F9 N5 O21 S3
Formula weight	1020.84
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.2229(16) A alpha = 104.325(3) deg.
	b = 11.4212(16) A beta = 104.679(3) deg.
	c = 13.2263(19) A gamma = 90.271(3) deg.
Volume	1584.9(4) A^3
Z, Calculated density	2, 2.139 Mg/m^3
Absorption coefficient	2.991 mm^-1
F(000)	1004
Crystal size	0.30 x 0.20 x 0.14 mm