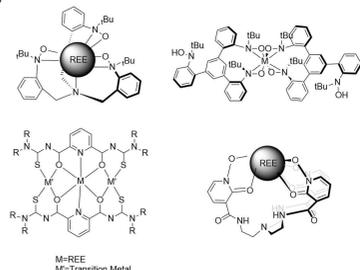


Background

- Rare Earth Elements (REE) are used in modern technology such as cellphones, laptops, and vehicles¹
 - Recovery methods of REEs include excessive mining, acid leaching, alkali fusion, and manufacturing^{2,3}
- Current methods of recycling REEs
 - Liquid - liquid or acidic extraction⁴
 - Inefficient and environmentally hazardous⁵
- Alternate strategy - chelating ligands (Figure 1)
 - Figure 1. Examples of Ligands used for REE Recovery.^{6,7,8,9}

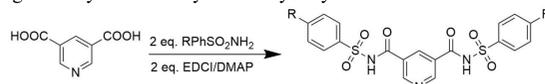


- No examples of nitrogen-based chelating ligands with sulfonamides

[NNN]-Pincer Ligands With Sulfonamides

- One known method to synthesize target pyridine acyl arylsulfonamide using a coupling agent (Figure 2).¹⁰
- What about microwave reaction conditions?
 - Make amide bonds without coupling agents under green, sustainable, cost efficient conditions

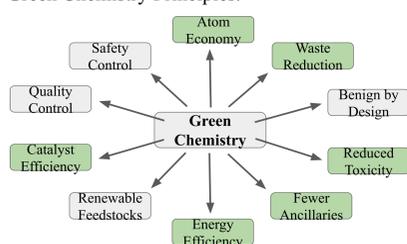
Figure 2. Synthesis of Pyridine Acyl Arylsulfonamides.¹⁰



Objectives

- Develop new methods to synthesize [NNN] pincer ligands and sulfonamide quinoline ligands utilizing green chemistry principles (Figure 3)
- Explore reactivity of REEs with library of bidentate and tridentate nitrogen-based sulfonamide ligands

Figure 3. Green Chemistry Principles.



[NNN]-Pincer Ligand Synthesis

Scheme 1. Microwave Synthesis of [NNN]-Pincer Ligands.

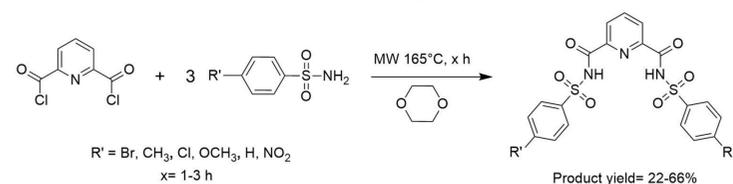
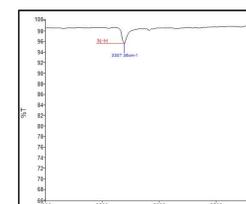


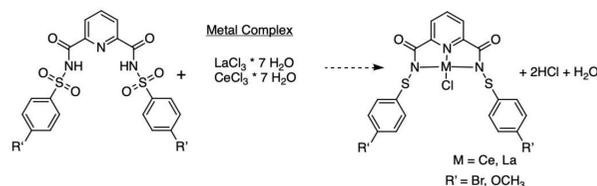
Figure 4. Portion of an IR Spectrum for NNN-Pincer Ligand R' = CF₃.



- Faster reactions occur with electron donating substituents
- Improved yields with electron rich sulfonamides
- NH stretch at ~ 3300 cm⁻¹ used to monitor reactions with REEs

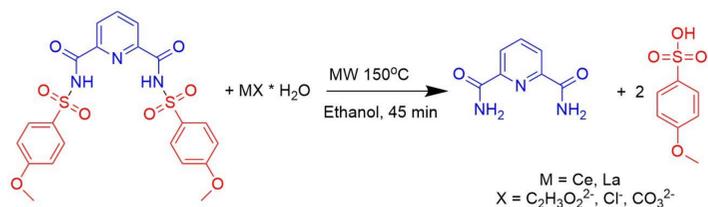
Reaction of [NNN]-Pincer Ligands with REEs

Scheme 2. Proposed Metalation Strategy between [NNN] Pincer Ligand and REEs.



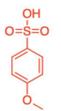
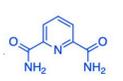
- Other REEs PrCl₃, Ce₂(C₂O₄)₃, Ce₂(CO₃)₃, and La₂(CO₃)₃ react similarly

Scheme 3. Reaction of [NNN]-Pincer Ligands with REEs.



- Broad IR stretch at 3347 cm⁻¹ consistent with an -OH group, overlaps -NH₂ stretch
- Sharp IR stretch at 1678 cm⁻¹ consistent with -C=O stretch of amide
- Disappearance of the ¹H NMR shift at 12.8 ppm supports cleavage of the sulfonamide bond (Table 1)
- ¹H NMR experimental data consistent with authentic samples of the pyridine diamide and sulfonic acid
- Observed degradation of [NNN] pincer ligand by hydrolysis

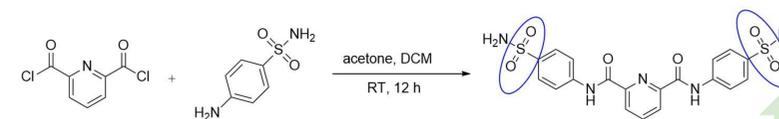
Table 1. Comparison of IR and ¹H-NMR Spectra in the Reaction of [NNN] Pincer Ligands with REEs.

Group Substituent	IR Stretch, Experimental	IR Stretch, Literature ¹¹	¹ H-NMR, Experimental
	broad, 3347 cm ⁻¹	broad, 3200 cm ⁻¹	- 7.0-8.0 ppm, two 2H doublets in aromatic region - 3H singlet at 4 ppm for -OMe
	- sharp, 1678 cm ⁻¹ - two sharp peaks, 3300 cm ⁻¹	- sharp, 1650 cm ⁻¹ - 3100-3300 cm ⁻¹	- disappearance of peak at 12.8 ppm - 3H multiplet at 8.2 ppm for pyridine

Redesign of [NNN]-Pincer Ligand

Strategy 1 - Strengthening the C-N bond to prevent hydrolysis

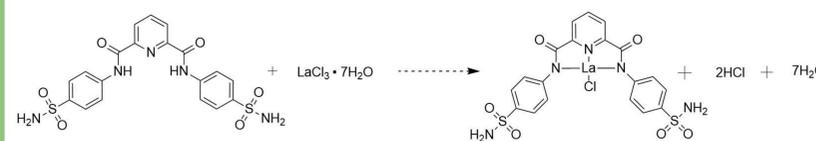
Scheme 4. Synthesis of [NNN]-Pincer Ligand with Moved Sulfonamide Groups.¹²



- Moving sulfonamide group away from coordinating pocket

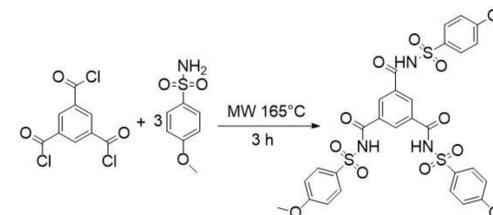
- Future work - examine reactivity of new NNN-pincer ligand with REEs

Scheme 5. Proposed Synthesis of Modified [NNN]-Pincer Ligand with REEs.



Strategy 2 - Trianionic [NNN] ligands

Scheme 6. Synthesis of Trianionic [NNN]-Pincer Ligand.

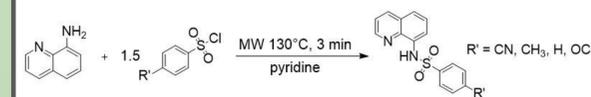


- IR spectrum shows one NH peak in the 3200-3300 cm⁻¹ region which indicates the change of -NH₂ to -NH consistent with sulfonamide bond formation
- The ¹H-NMR and IR spectra show differences between starting materials and final product and are consistent with the proposed product
- Future work - purify ligand and coordinate to REEs

Bidentate Quinoline Sulfonamide Ligands

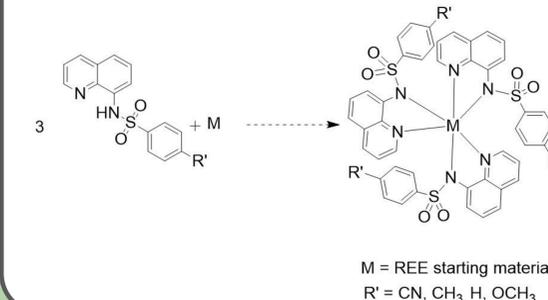
- Evaluate differences in coordination of tridentate and bidentate ligands to REEs
 - Gain a better understanding of the electronics of REE complexes with bidentate vs. tridentate ligands

Scheme 7. Synthesis of Quinoline Sulfonamide Ligands.¹³



Future Work

Scheme 8. Coordination of Quinoline Sulfonamide Ligands to REEs.



Conclusions

- Developed greener methodology for synthesis of the pyridine acyl arylsulfonamides [NNN]-pincer ligands using microwave conditions
- REE metalation reactions support ligand hydrolysis
- Redesigned the ligand to strengthen the C-N bond and to investigate trianionic scaffolds to better support +3 REEs
- Quinoline sulfonamide ligands were synthesized and coordination with REEs is underway

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