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Synthesis and Spectroscopic Investigation of Substituted Salen and Phthalocyanine Chelating Ligands

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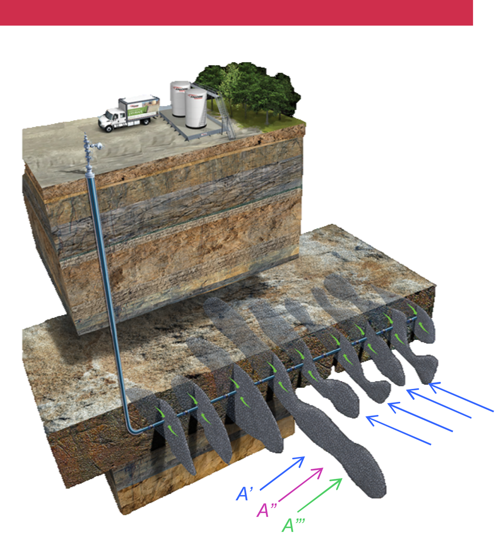
Introduction

Subterranean geothermal and shale-oil wells reside several kilometers below the surface of the earth. Currently, few viable fluid flow tracking methods exist that can accurately monitor and examine long-term fluid flows. When wells are opened, there are several paths of fluid-flow which need to be monitored. The use of porous ceramic proppants loaded with molecular "taggants" has been proposed as a viable method of tracking close proximity wells with accuracy and relative ease. Through the use of easily accessible spectroscopic properties these molecular "taggants" can be monitored at the surface and give information about the underground fluid flow behavior.



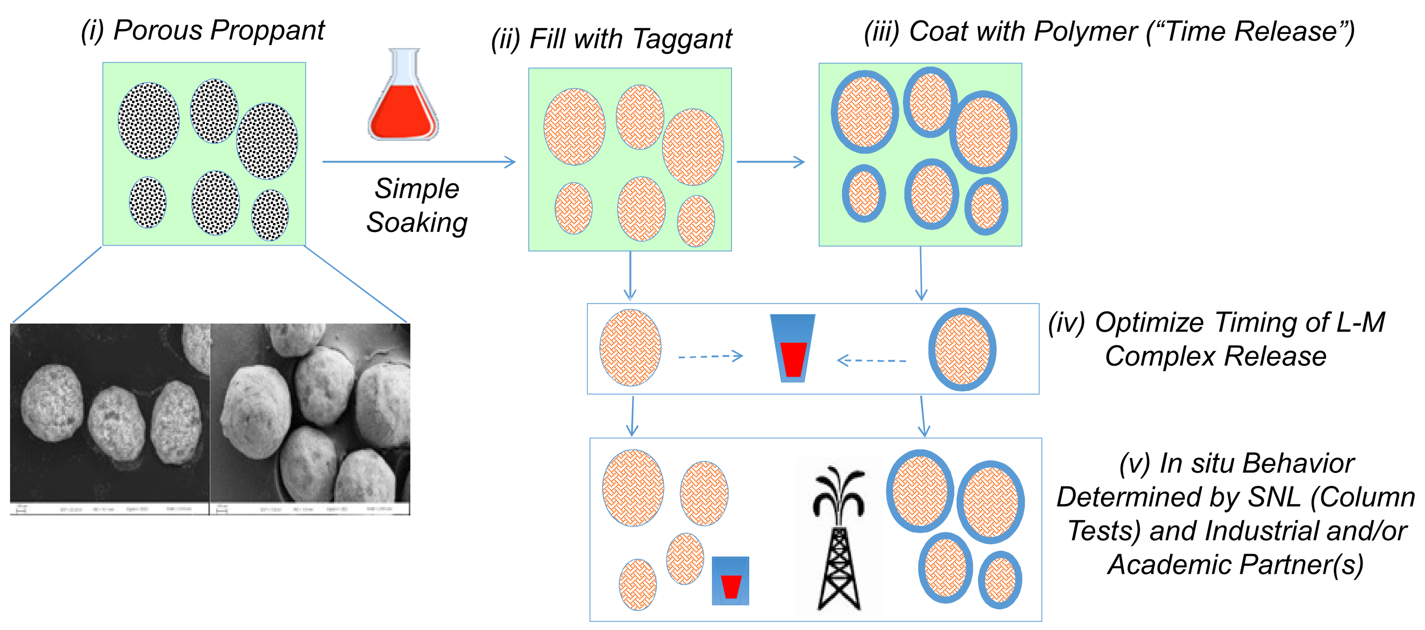
Schematic of an underground well

Commercially available ceramic proppant

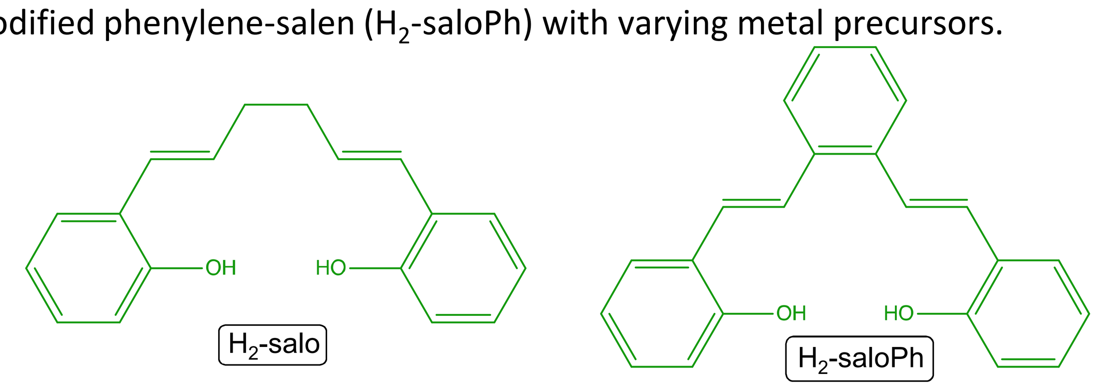
In this effort, metal salen [M(salo-R)] complexes were investigated as potential "taggants". Initial results indicated that these types of compounds have the physical properties that will survive the underground conditions and also have exhibit distinct spectroscopic properties, which should allow for accurate detection.

Approach

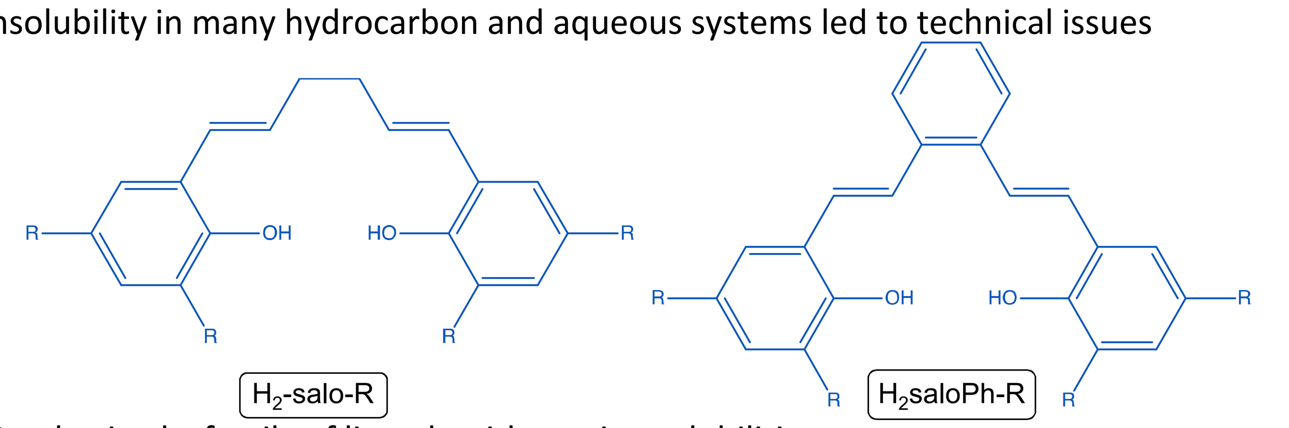
Ceramic proppants can be loaded with molecular "tags" for accurate fluid-flow monitoring, subsequent sealing of these porous proppants allows for < 1 year monitoring.



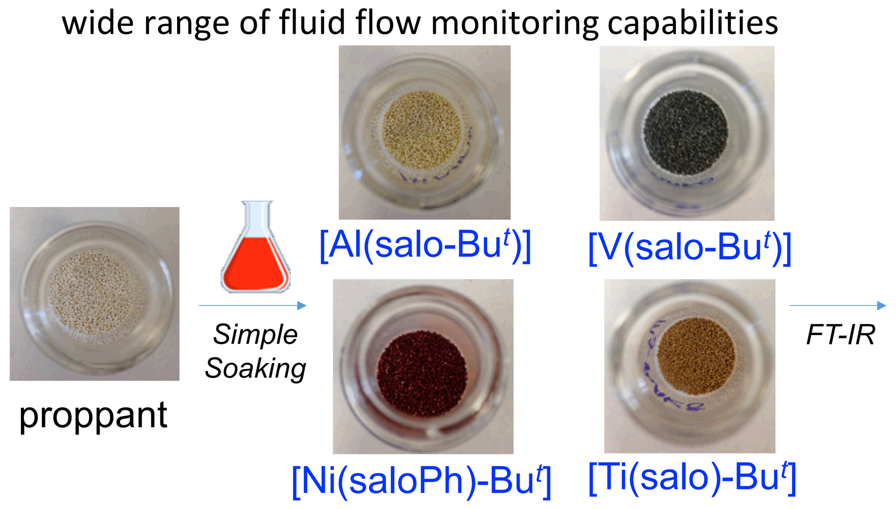
Initial studies examined the coordination chemistry of commercially available salen (H_2- salo) and modified phenylene-salen (H_2-saloPh) with varying metal precursors.

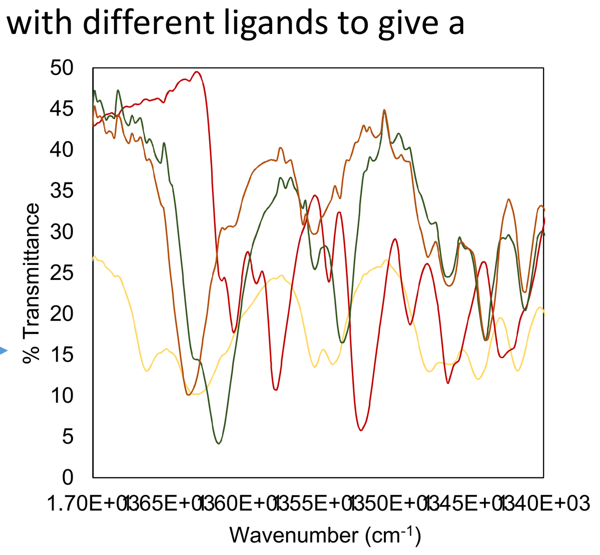


- Showed differential spectroscopic properties when coordinated with different metals
- Insolubility in many hydrocarbon and aqueous systems led to technical issues



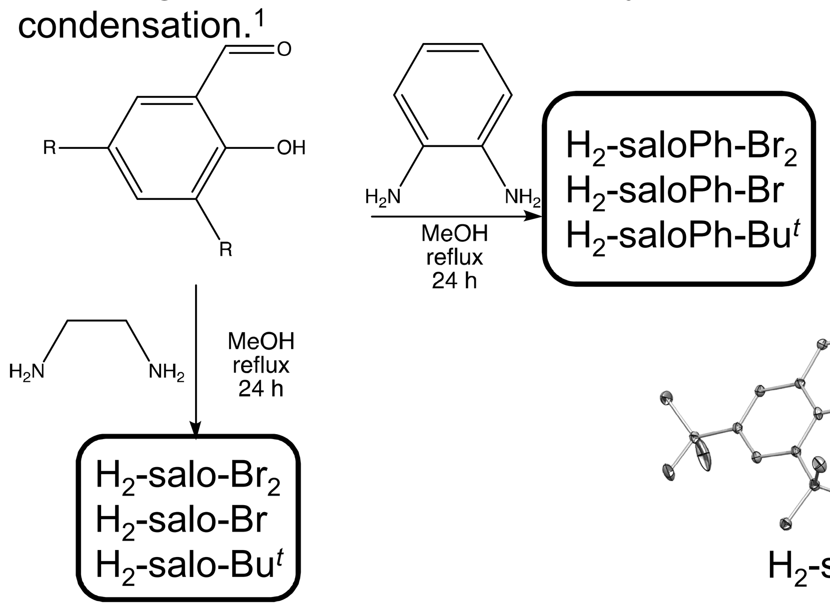
- Synthesized a family of ligands with varying solubilities
- Synthesized a family of metal coordination complexes with different ligands to give a wide range of fluid flow monitoring capabilities

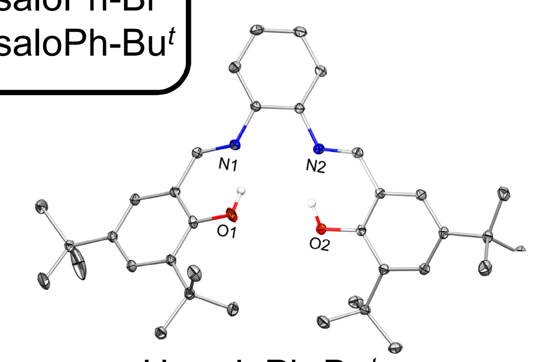




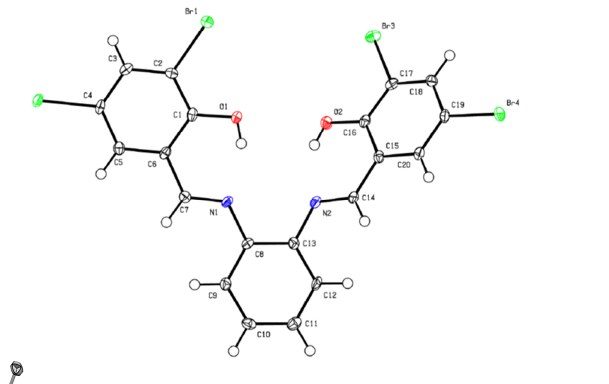
General Ligand Synthesis

Following established routes, a family of salen derivatives was synthesized by an aldehyde amine condensation.[1]

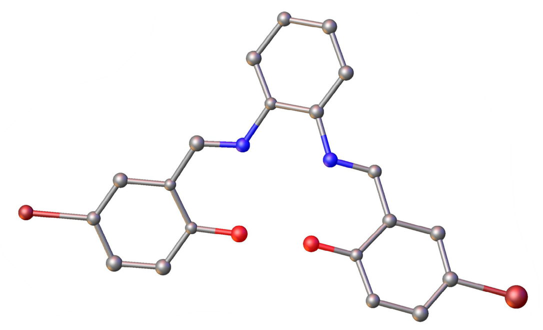




H_2-saloPh-Bu^t



H_2-saloPh-Br$_2$



H_2-saloPh-Br

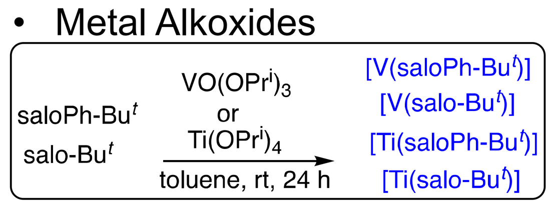
Compounds characterized by a variety of techniques, including [1]H NMR, [13]C NMR, elemental analysis, FT-IR, Raman and single-crystal X-ray analysis. Ligands containing an ethylene bridge instead of the shown phenylene bridge were also synthesized and fully characterized.

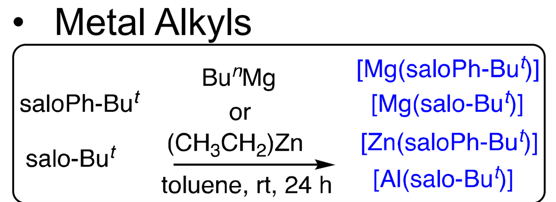
1: Darensbourg, D. J., et al. (2004) *Inorg. Chem.* **43**, pp. 6024-6034.

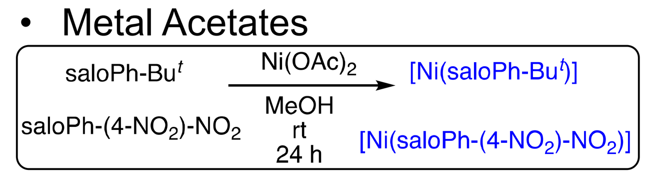
Metal Coordination

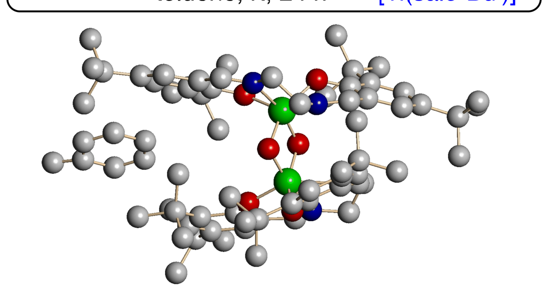
We synthesized a family of compounds focusing on first row transition metals. Coordination complexes have been synthesized from the in-house prepared H_2-saloPh-Bu^t and H_2-salo-Bu^t ligands.

- Metal Alkoxides
- Metal Alkyls
- Metal Acetates



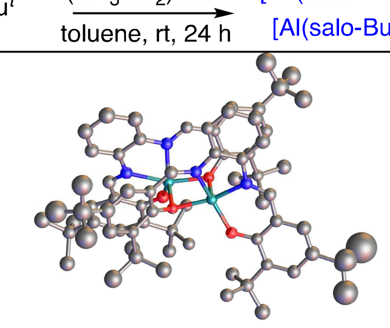






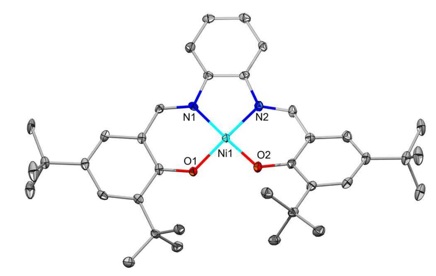
[Ti(salo-Bu^t)]$_2$

Dimer with a 7-coordinate titanium atom due to a double-oxo bridge and Ti=O bonding



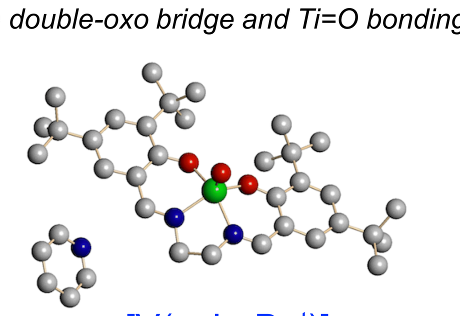
[Mg(saloPh-Bu^t)]$_2$

Solved as a dimer with a 5-coordinate magnesium species bound to N, O and bridged via O



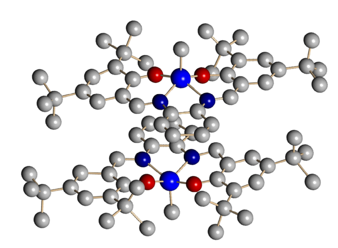
[Ni(saloPh-Bu^t)]

Exists as a monomer with a 4-coordinated nickel species



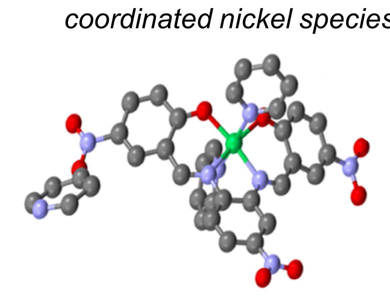
[V(salo-Bu^t)]

Monomeric structure with a 6-coordinate vanadium atom due to V=O bonding



[Al(salo-Bu^t)]$_2$

Monomer with a 5-coordinate aluminum bound to N, O and C



[Ni(saloPh-(4-NO$_2$)-NO$_2$)]

Monomer with a 6-coordinate nickel bound to N and O and solvated in pyridine

Structures have been solved for the following alkali earth, transition, and post transition metals: Mg, Ca, Sc, Ti, Zr, Hf, V, Co, Ni, Zn, Al, Ga, In and Tl

Stability Testing

Long term fluid flow monitoring requires chemical inertness under harsh conditions.

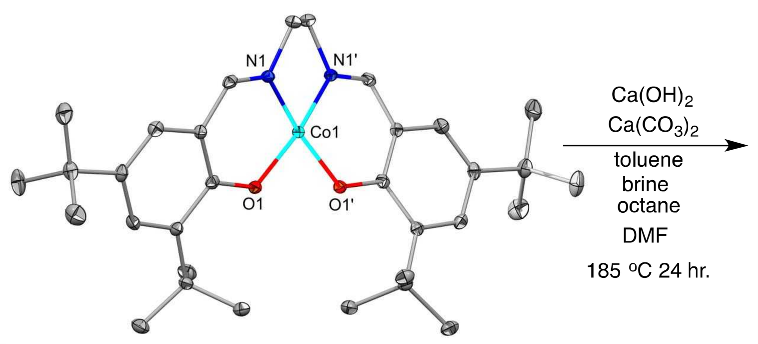
- Testing includes high temperature and pressure conditions of 185 ^oC, 3 atm, which are present in geothermal and shale oil wells.
- Additionally, metal ions are present underground in the form of hydroxides and carbonates (among other salts) and could potentially exchange with the coordinated metal in the tracer ligands.
- All current metal coordination complexes were tested in a wide range of solvents: DMF, toluene, brine, octanes. Acidic and basic conditions were also explored.

Inert:

-[Co(salo-Bu^t)]
-[Ni(saloPh-Bu^t)]
-[V(saloPh-Bu^t)]
-[V(salo-Bu^t)]
-[Ti(salo-Bu^t)]
-[Ti(saloPh-Bu^t)]
-[Zn(saloPh-Bu^t)]
-[Zn(salo-Bu^t)]

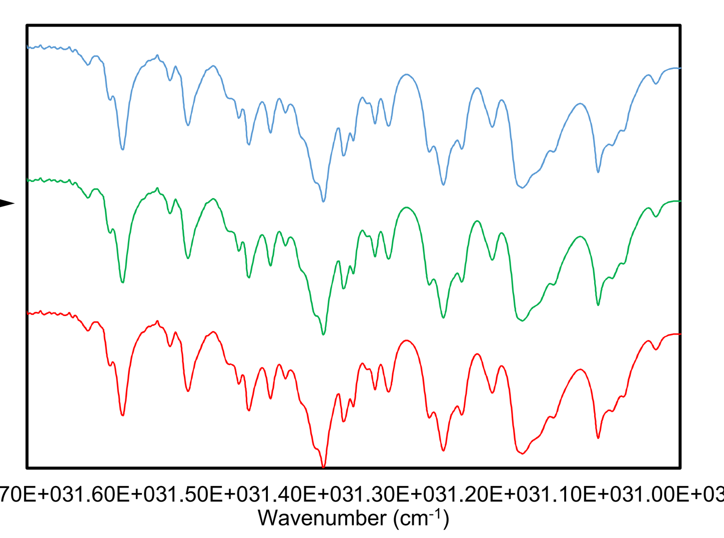
Reactive*:

-[Al(salo-Bu^t)]
-[Al(saloPh-Bu^t)]



[Co(salo-Bu^t)]

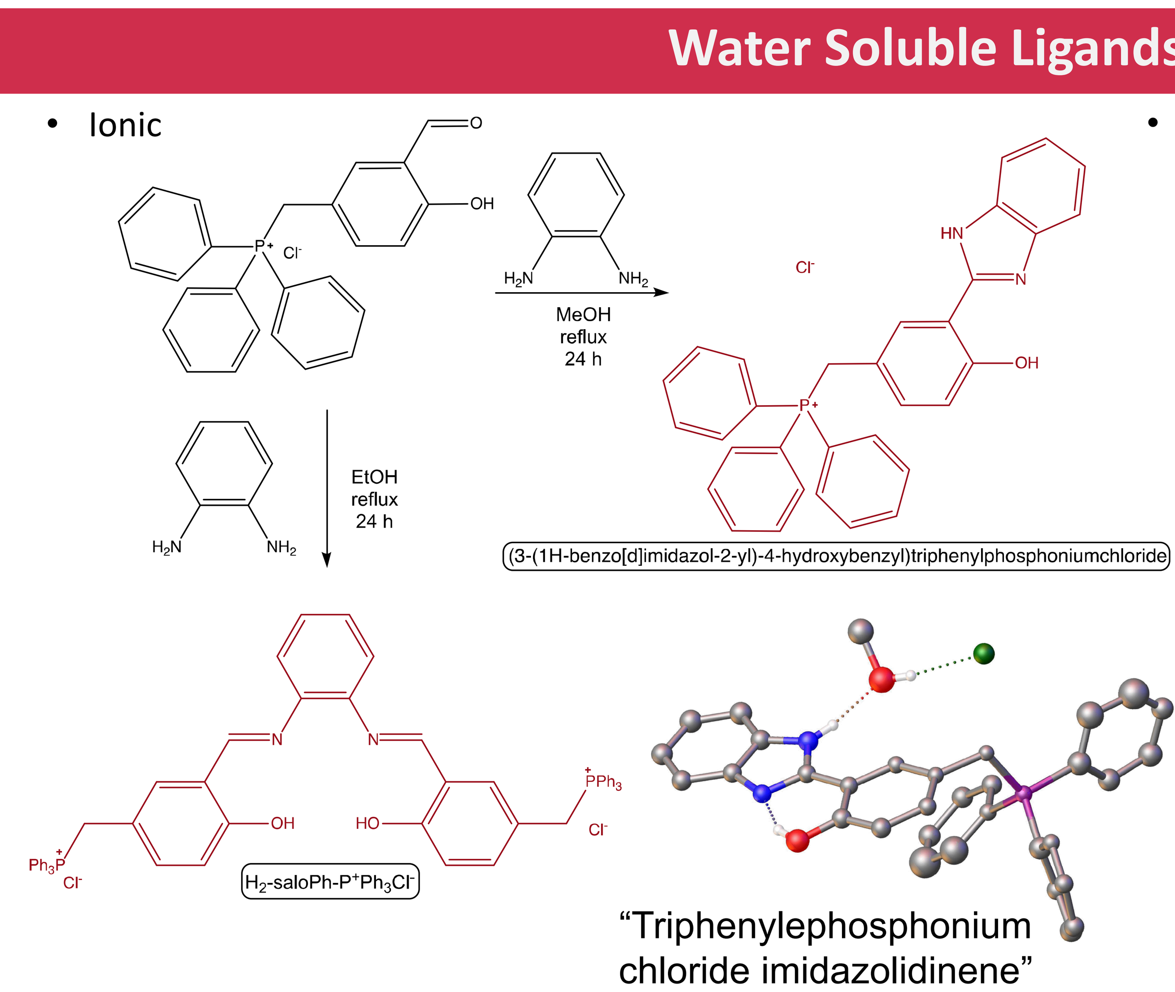
**Likely reasons for reactivity are electronic properties of aluminum and its affinity for oxygen*



[Co(salo-Bu^t)] and two representative exchange reactions clearly demonstrates no reaction occurs

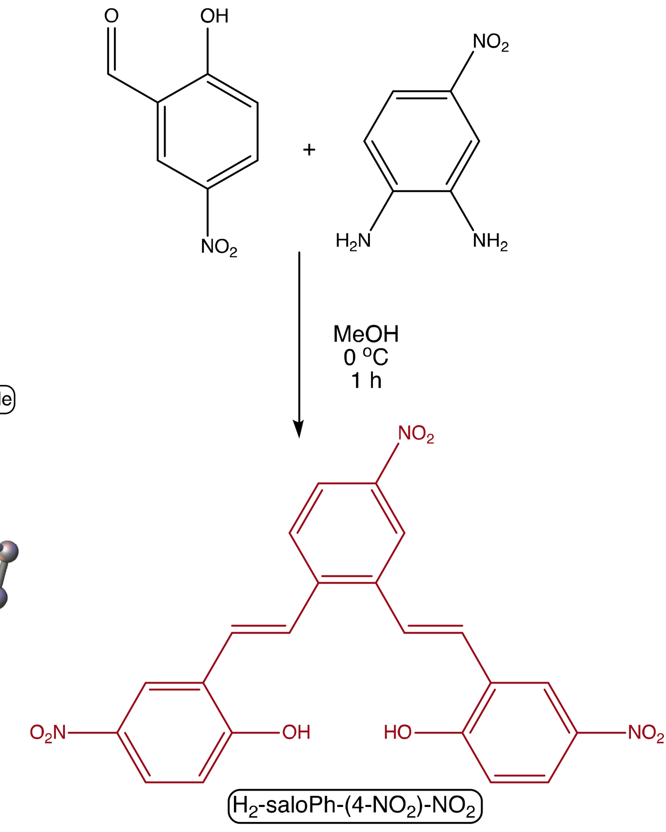
Water Soluble Ligands

- Ionic



"Triphenylephosphonium chloride imidazolidinene"

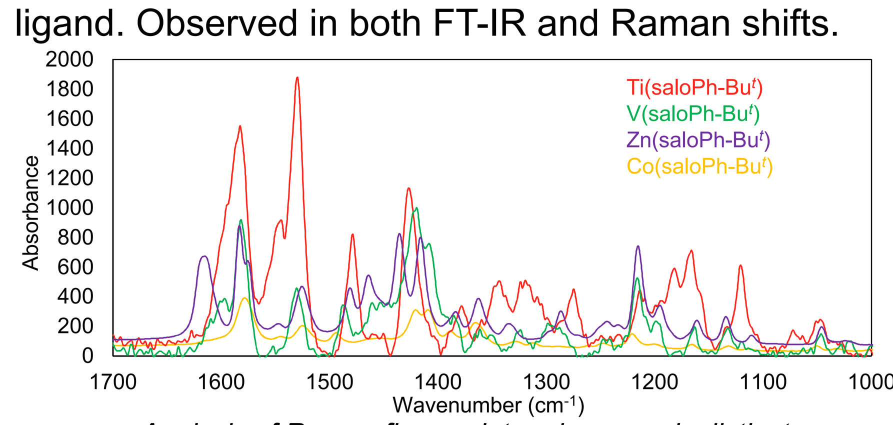
- Non-ionic



Both ionic and non-ionic routes featured interesting imidazolidine ring formation chemistry as unwanted side products.

Spectroscopy

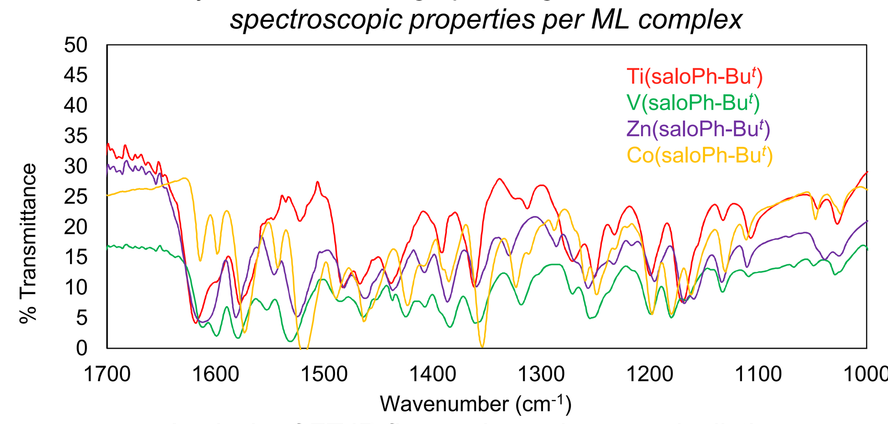
The compounds demonstrated unique spectroscopic shifts dependent upon the coordinated metal, and ligand. Observed in both FT-IR and Raman shifts.



Analysis of Raman fingerprint region reveals distinct spectroscopic properties per ML complex

Metal	M(saloPh-Bu^t) C=N shift (cm^{-1})	M(salo-Bu^t) C=N shift (cm^{-1})
[redacted]		
V	1581.78	1612.88
[redacted]		
Zn	1615.21	1621.88

Raman C=N shifts detail unique signals for different metals and ligands



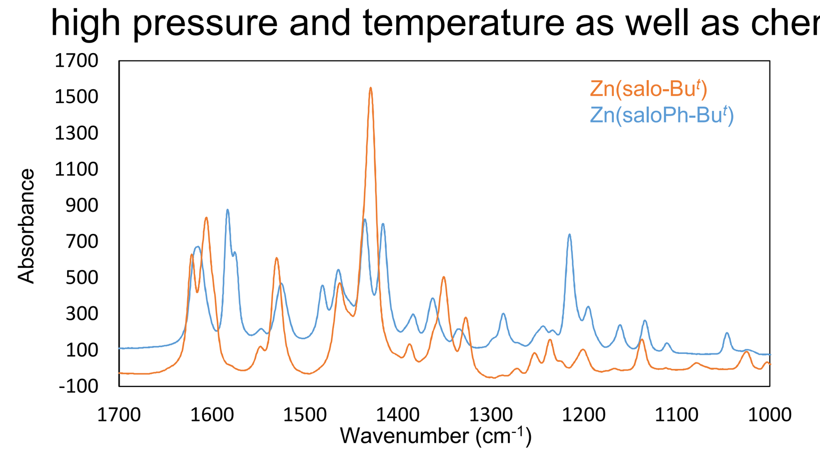
Analysis of FT-IR fingerprint region reveals distinct spectroscopic shift per ML complex

Metal	M(saloPh-Bu^t) C=N shift (cm^{-1})	M(salo-Bu^t) C=N shift (cm^{-1})
[redacted]		
V	1599	1616
[redacted]		
Zn	1612	1607

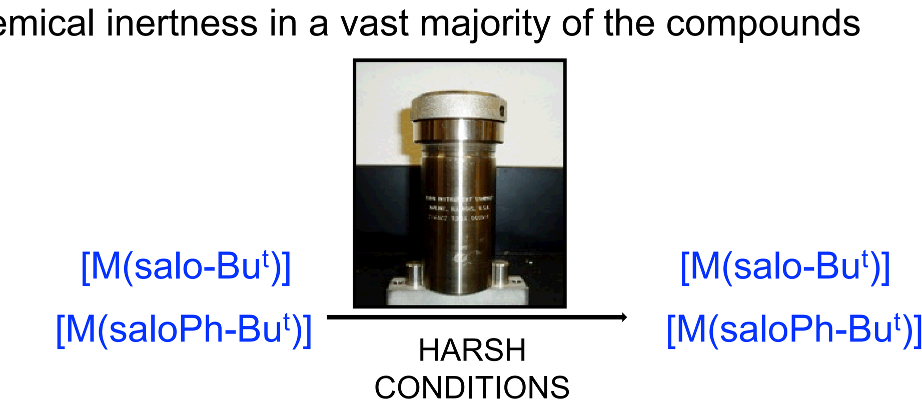
FT-IR C=N shifts detail unique signals for different metals and ligands

Summary and Future

- Families of substituted metal salen complexes have been synthesized and well-characterized for possible use as molecular tracers for subterranean fluid flow monitoring
- Testing in DMF/toluene/octanes/brine/acidic and basic aqueous systems demonstrates stability under high pressure and temperature as well as chemical inertness in a vast majority of the compounds



Raman spectrum of Zn coordination complexes of salo-Bu^t and saloPh-Bu^t ligands indicate differences in C=N stretches not only from metals but also ligands of the same coordination metal



Metal coordination compounds are chemically inert under conditions potentially present in shale-oil and geothermal wells

- Fluid-flow elution kinetics currently being tested in ISOPAR-G and aqueous systems

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