Synthesis and Characterization of Metal-Salen Complexes for Underground Fluid Flow Tracking

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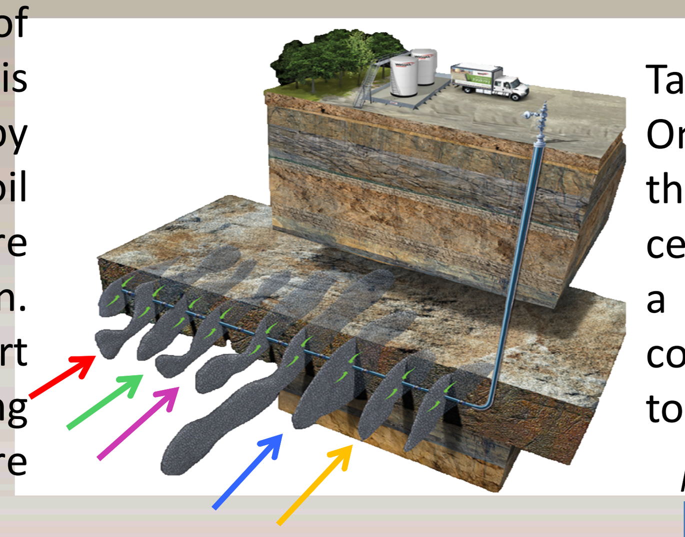
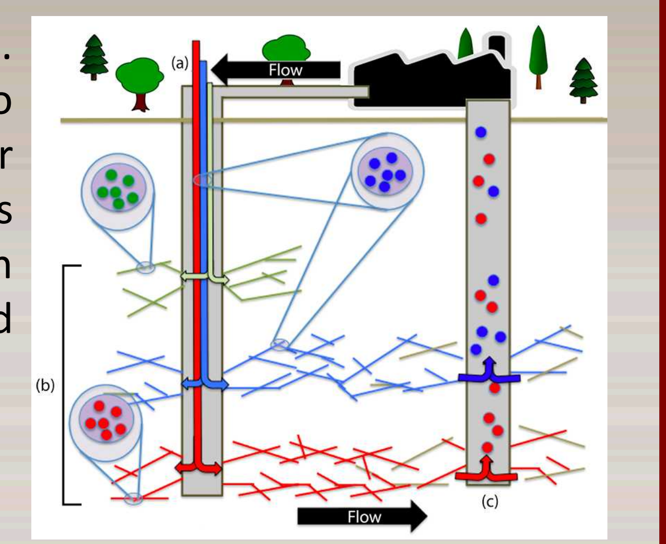
Long term tracking of underground fluid flows is of continued interest by geothermal and oil companies for more efficient energy extraction. This research effort focused on developing tags to accurately measure flow in fracked oil wells.

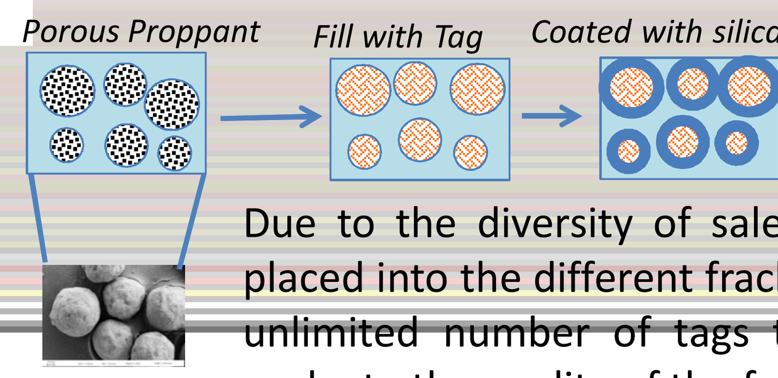


The approach was to synthesize tags that can be easily identified by diverse spectroscopic properties but also will be soluble in either water or organic solutions and withstand the high pressure of deep underground wells.

Introduction

Tags developed for this project are based on metal-salen complexes. Once synthesized, they were intercalated into proppants for delivery to the wells. Proppants are a porous solid material such as artificial sand or ceramic of 106 µm – 2.36 mm in size. Proppants are coated with silica as a time release mechanism for the tags. Over time, the metal-salen compounds are expected to be released into the fluid flow underground to separate zones and then collected at the surface.

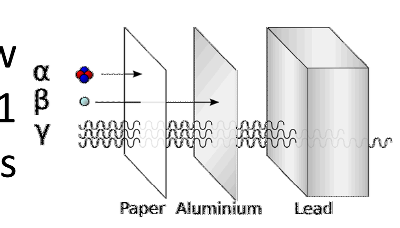




Due to the diversity of salen compounds and metals available, different tags will be placed into the different fracks. The unique signatures of these compounds allows for an unlimited number of tags to be used. The zones can be monitored individually to evaluate the quality of the fracking wells.

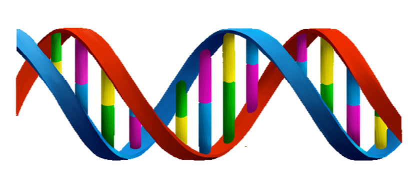
Previous attempts of tracers for fluid flow

- **Radioisotopes**: Pervious efforts to track flow include radioisotope tracers such as iodine 131 (releases gamma and beta) and tritium (releases alpha).



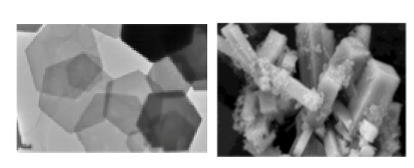
Wiebenga, W. A.; Ellis, W. R.; Seatonberry, B. W.; Andrew, J. T. G. Radioisotopes As Groundwater Tracers. *Journal of Geophysical Research* **1967**, *72* (16), 4081–4091 DOI: 10.1029/JZ072i016p04081.

- **DNA**: There has also been efforts using DNA fragments as tracers.



Ritter, S. K., *Chemical & Engineering News* **2014**, *92*, 31-33.

- **Nanoparticles**: Particles of metal oxides were also investigated as potential tracers.

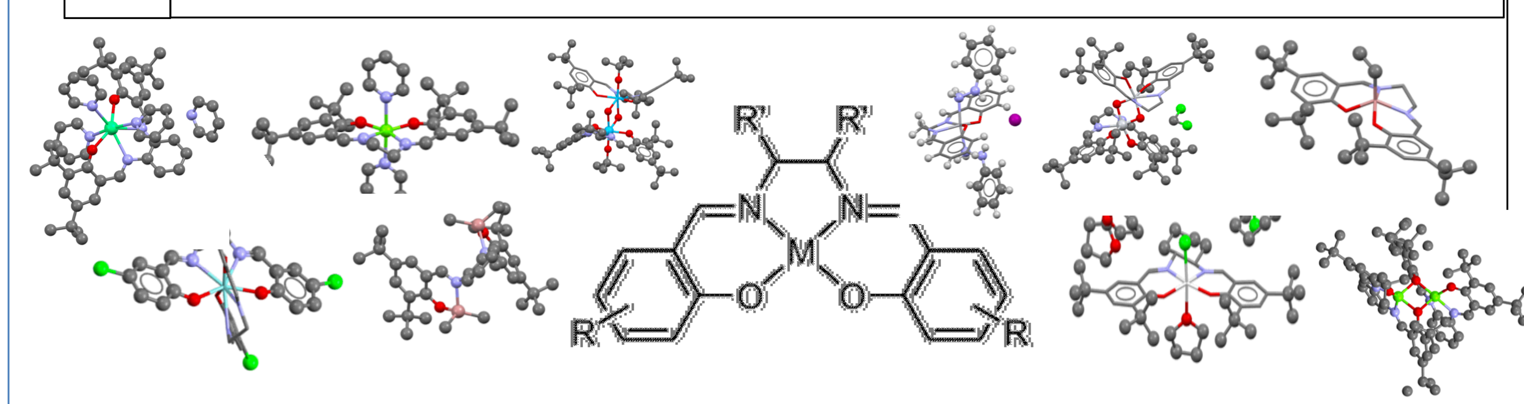


Kemp, R. A.; Hess, R. F. http://energy.gov/sites/prod/files/2015/06/f23/Track3_EGS_1.4_Sandia-CARBO-PIKemp.pdf "Tagged Nanoparticles for Fluid Flow Monitoring".

Desirable properties for tags include the ability to withstand high temperature and pressure and wont bind to material in the environment of wells is desirable for tracers so they can be analyzed when resurfaced.

Metal-Salens have been extensively studied and reported in literature. Where to start?

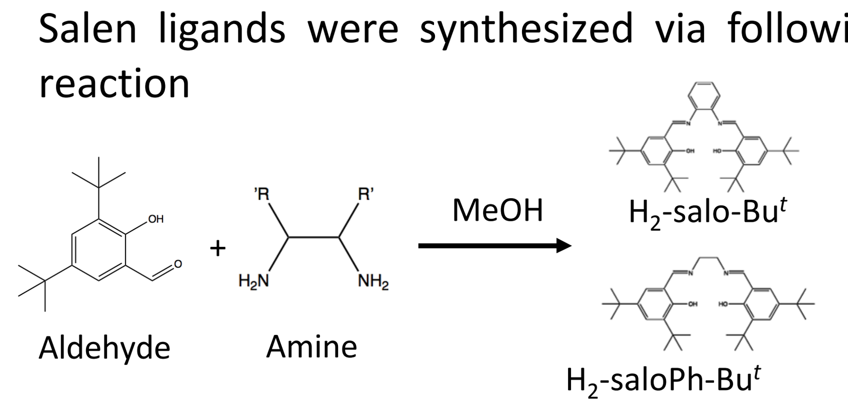
Mg	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Ga	In	Tl
8	6	8	46	138	44	783	230	287	386	572	207	87	12	13	0



Numerous metal-salen complexes have been reported in literature from across the periodic table using a variety of substituted salens. The value below the metal (above) corresponds to the number of structures reported for the first row metals. Due to our previous work on group 2 metal salen complexes and the large quantities of complexes that exist with the first row transition metals, group 13 was chosen as the area of focus.

Metal-Salen synthesis approach

Salen ligands were synthesized via following reaction

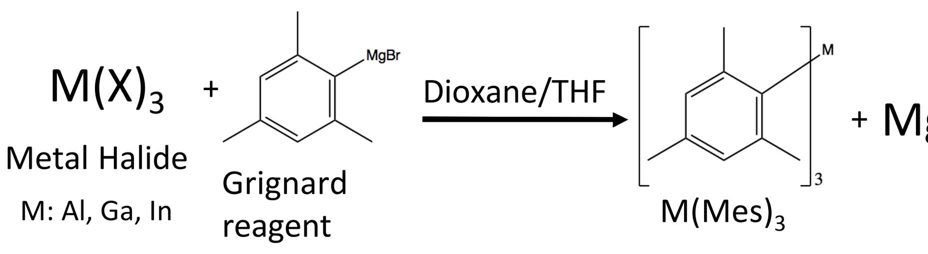


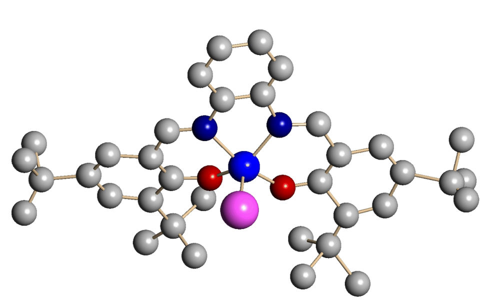
General synthesis for metal-salens

$$M(L)_x + H_2\text{-saloR-Bu}^t \xrightarrow{\text{Toluene}} M(\text{saloR-Bu}^t) + x\ \text{H-L}$$

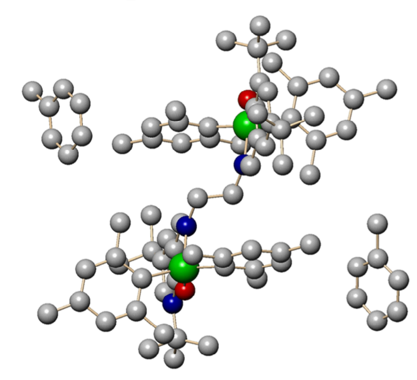
M: Al, Ga, In, Tl
L: Mes, OEt

Mesityl precursors were synthesized via following reaction

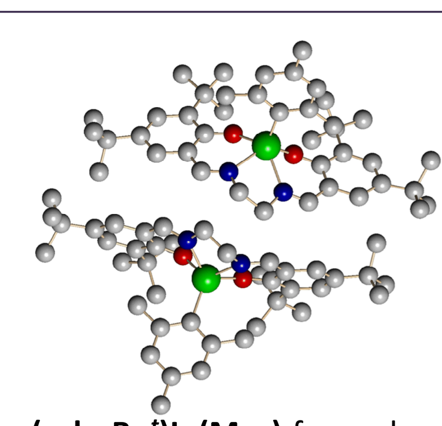




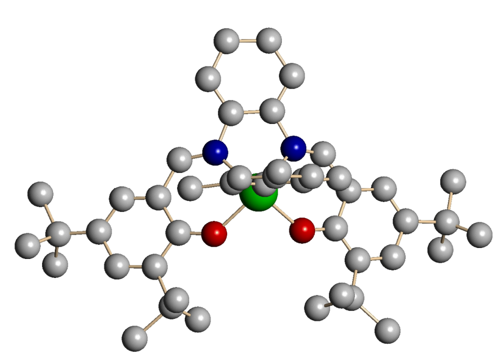
(saloPh-Bu^t)AlBr formed a 1:1 monomer with a halogen contaminant



(salo-Bu^t)Ga$_2$(Mes)$_4$ formed a 2:1 monomer with two mesityl groups bound to metal



(salo-Bu^t)In(Mes) formed a 1:1 monomer with one mesityl group bound to the metal



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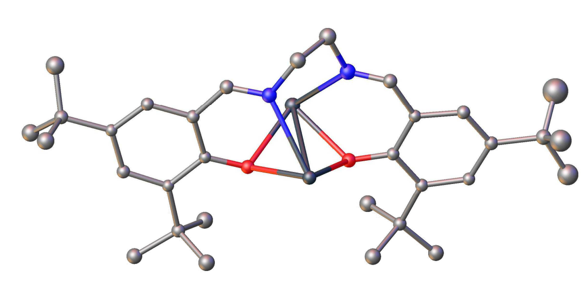
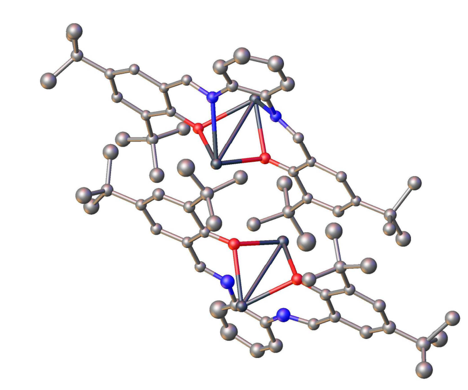


(salo-Bu^t)Tl$_2$ formed a 2:1 monomer with interesting Tl-Tl interactions



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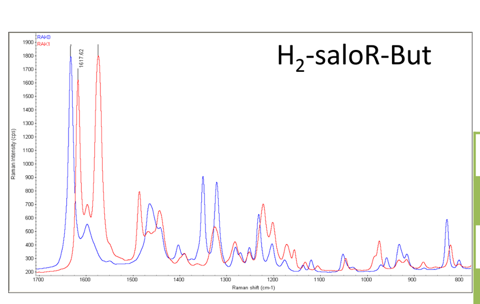
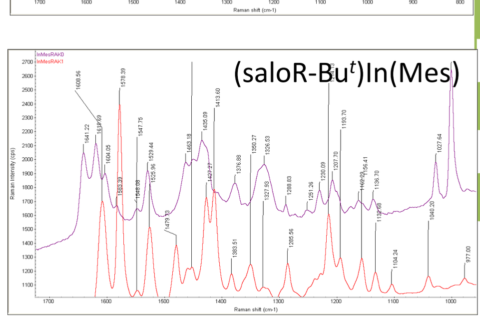
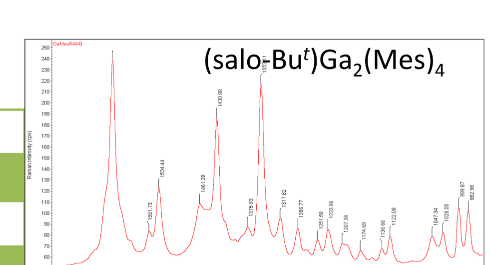
Infrared and Raman Spectroscopy analysis indicates a distinction of the metal-salens

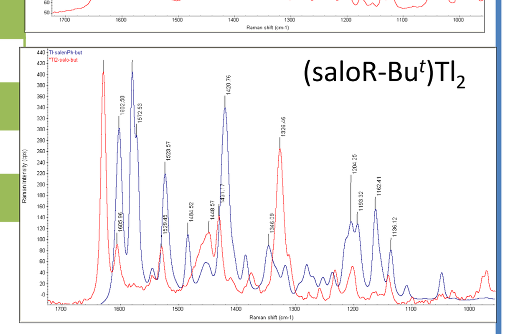


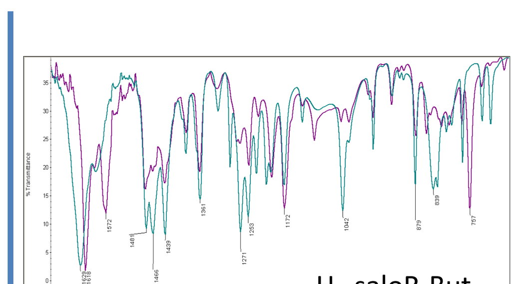


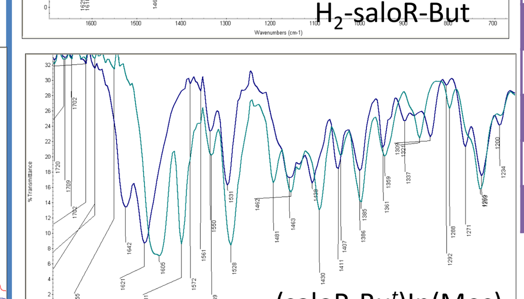
Raman spectra

Compound	C=N (cm^{-1})
H$_2$-Salo-But	1633
H$_2$-SaloPh-But	1618
(salo-Bu^t)Ga$_2$(Mes)$_4$	1617
(salo-Bu^t)In(Mes)	1620
(saloPh-Bu^t)In(Mes)	1609
(salo-Bu^t)Tl$_2$	1629
(saloPh-Bu^t)Tl$_2$	1603



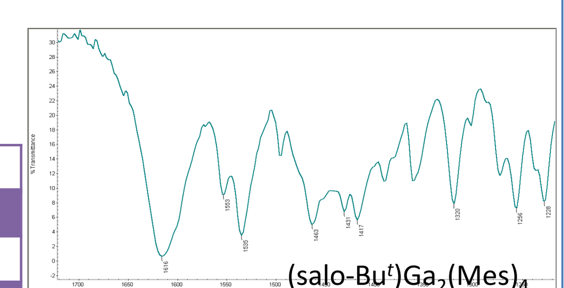


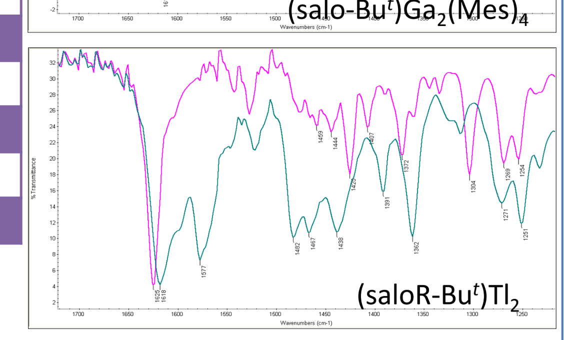




FT-IR spectra

Compound	C=N (cm^{-1})
H$_2$-salo-But	1629
H$_2$-saloPh-But	1618
(salo-Bu^t)Ga$_2$(Mes)$_4$	1616
(salo-Bu^t)In(Mes)	1621
(saloPh-Bu^t)In(Mes)	1605
(salo-Bu^t)Tl$_2$	1625
(saloPh-Bu^t)Tl$_2$	1618



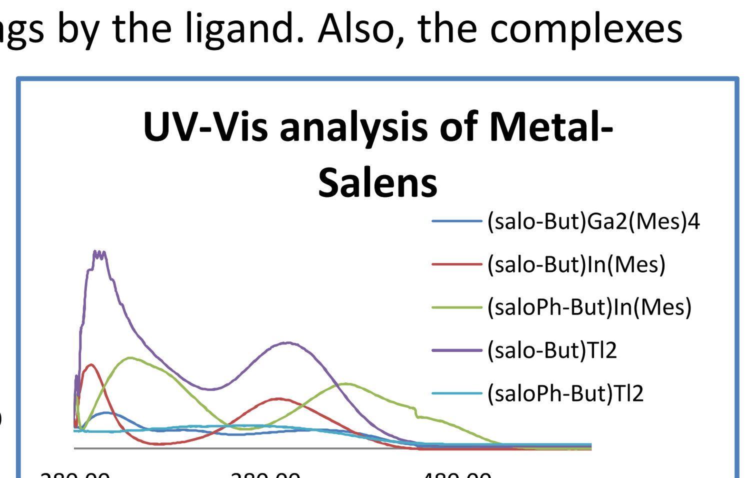


Analysis of metal-salens and salen ligands using Raman and IR spectroscopy show that it is possible to distinguish the ligand to the metal complexes by the carbon to nitrogen stretch in the molecule. In addition to this, there is a varying shift between metal complexes with the same ligand but different metal and also between same metal and different ligand. This gives allows us to pinpoint which metal complex is present in a sample by two simple spectroscopy methods.

UV-Vis Spectroscopy was performed for further analysis in order to be able to distinguish the complexes

Compound	Wavelength (nm)
H$_2$-saloPh-but	347
H$_2$-salo-but	344
(salo-Bu^t)Ga$_2$(Mes)$_4$	297, 403
(salo-Bu^t)In(Mes)	289, 387
(saloPh-Bu^t)In(Mes)	309, 422
(saloPh-Bu^t)Tl$_2$	323, 469
(salo-Bu^t)Tl$_2$	295, 392

UV-Vis shows that there is a shift in λ_{max} from the free ligand to their corresponding metal-complex. The complexes with same metal and different ligand also have different shifts which indicates that is it possible to distinguish the tags by the ligand. Also, the complexes with same ligand and different metal have different shifts indicating it is possible to distinguish them by metal. Both absorptions in the metal complexes are from metal to ligand charge transfer.



Summary

- A family of group 13 metal salen complexes have been synthesized.
- Three different spectroscopy analysis shows the ability to distinguish the complexes from each other.
- Modeling and stability tests will be conducted on the novel compounds to see how they will interact with other material in fluid wells and to see if they will survive harsh pressure environments.

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