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# Manganese Nanoparticles Synthesis for 3D Printing Applications

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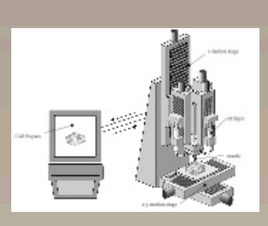
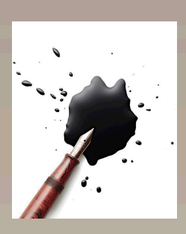
## Introduction

Direct write manufacturing is a method that provides precision for 3D printing. Currently, silver nanoinks are in demand due to silver's high conductivity. However, silver is very expensive, so there are more research pursuing cost competitive substitutes. Silver is also incompatible with many commercial products, which creates many problems in the production line. In addition, it costs producers $0.63 for every gram of silver, which is significantly more expensive than manganese, which stands at $0.017 per gram. Manganese conductivity stands at $6.2\times10^5$ S/m while silver stands at $6.2\times10^7$ S/m.



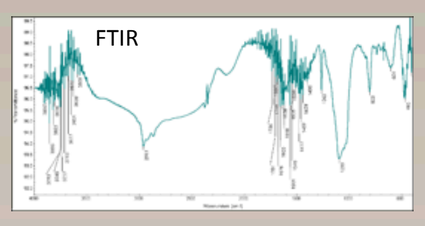


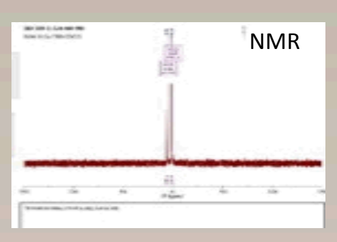

Exploration on precursor synthesis are being pursued for the most efficient route to produce stable manganese nanoparticles. We are looking at the bond strength between Mn-O, Mn-C, Mn-Cl, and Mn-N while using them as precursors for nanoparticle synthesis.

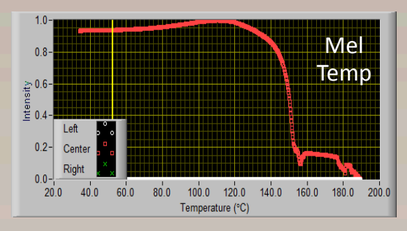
## Manganese Mesityl (Mn-C bond)

Manganese mesityl is synthesized from the reaction of manganese(II) bromide and mesityl magnesium bromide in THF/Dioxane. The reaction is washed with hexane and extracted with toluene.

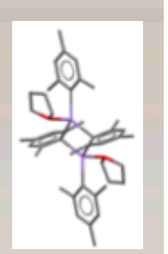
$$MnBr_2 + 2\ MgBr\text{-}Mes \longrightarrow Mn(Mes)_2 + 2\ MgBr_2$$



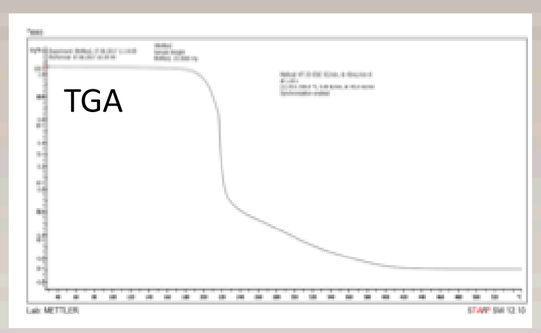




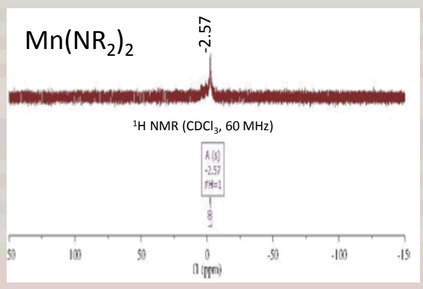

Thermal analyses of these compounds were initiated. The initial study of $Mn(Mes)_2$ appears to be within a useful temperature range for nanomaterial production (solvothermal (SOLVO) and solution precipitation (SPPT).

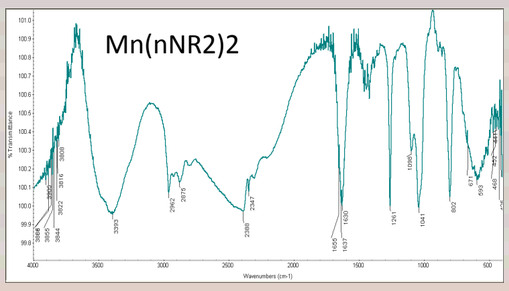


(THF)$Mn(Mes)_2$




## Manganese Amide (Mn-N bond)




$$MnBr_2 + 2\ K(NR)_2 \xrightarrow{THF} Mn(NR_2)_2 + 2\ KBr_2$$

Manganese amide was synthesized using the precursor potassium amide and manganese(II) bromide. NMR characterization was conducted on the final sample. One peak was preent at -2.57 ppm.

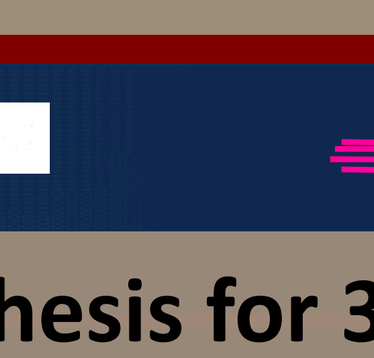
$$MnCl_2 + 2\ LiNR \xrightarrow{THF} MnNR_2 + 2\ LiCl$$

The $Mn(NR_2)_2$ produced was characterized with FTIR instrumentation. Since manganese is paramagnetic, further analysis will be required to determine the compound's properties.

## Manganese Alkoxides (Mn-O bond)

Manganese alkoxides are synthesized from the reaction of Mn(Mes)2 with a series of six aryl alcohols. The reactions are then left to slow evaporate in the glovebox to grow crystals.

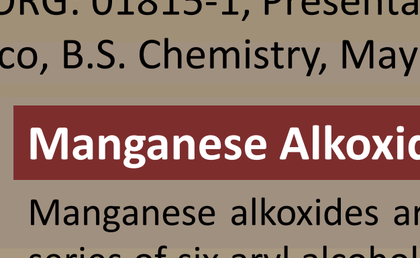
$$Mn(Mes)_2 + 2\ H\text{-}Oar \longrightarrow Mn(OR)_2 + 2\ H\text{-}Mes$$

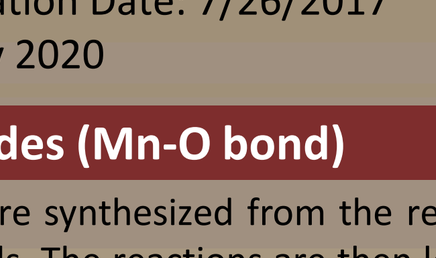


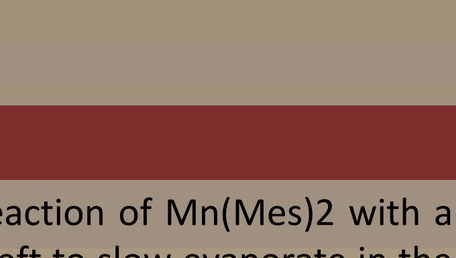
[Mn4(oMP)4py]·HoMP·3py
(H-oMP) o-cresol

[Mn(*o*PP)$_2$py]·HoPP·2py]
(H-oPP) 2-isopropylphenol

[Mn(DBP)(thf)]
(H-DBP) 2,6-di-tert-butylphenol





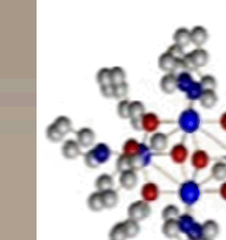


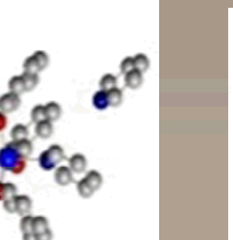
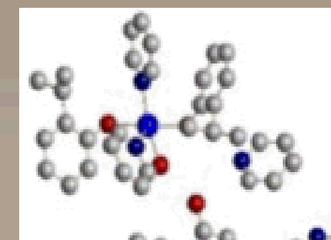

Single crystal x-ray analysis were conducted on the manganese alkoxides in addition to FT-IR and NMR.

## Nanoparticle Synthesis

### Manganese NP from MnMes2

$Mn(Mes)_2$ with Hex/Oct




$Mn(Mes)_2$+ HDA+ OCT → MnNP

*$Mn(Mes)_2$ dissolved in excess OCT added to HDA at 300°C. heated for 10 min.*

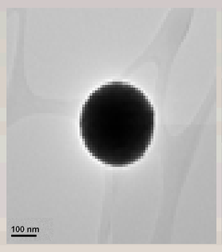
$Mn(Mes)_2$+HDA → MnNP

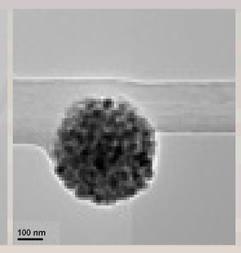
*$Mn(Mes)_2$ and HDA heated to 300°C. and held for 10 min.*

The reaction was heated to 300°C and held at that temperature for 10 minutes. The nanoparticles were amorphous through PXRD characterization. TEM imaging shows amorphous and agglomerated particles.

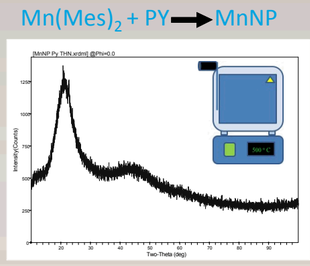
$Mn(Mes)_2$ + XY → MnNP

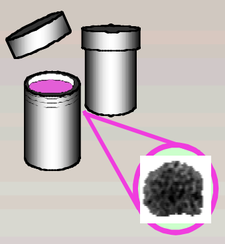
$Mn(Mes)_2$ with PY



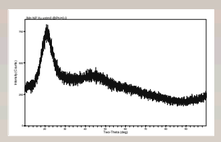



$Mn(Mes)_2$ + PY → MnNP

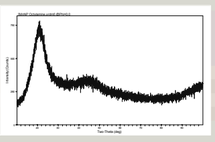




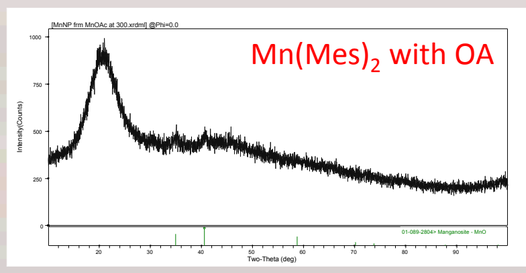
*Mn(Mes)2 and different solvents in a Parr bomb @180 °C for 24 h.*



$Mn(Mes)_2$ + OCT → MnNP



The reaction was heated to 180°C and held at that temperature for 24 hours. The nanoparticles were amorphous through PXRD characterization. TEM imaging shows circular particles that clumped up together.




Manganese acetate was reacted with 2 equivalence of oleic acid and heated up to 300°C and held for 20 minutes. PXRD analysis shows that MnO formed. This route is similar to the one found in literature from JACS.[1]

1. Bondi, J. F., Oyler, K. D., Ke, X., Schiffer, P., & Schaak, R. E. (2009). Chemical Synthesis of Air-Stable Manganese Nanoparticles. Journal of the American Chemical Society

## Summary and Next Steps

- The synthesis of metal nanomaterials provide new capabilities for printing microcircuits and other electronic applications.
- Manganese nanomaterials is beneficial due to the fact that it is more cost effective compared to silver.
- Solution precipitation of Mn(Oac) shows promise in producing MnO NP. Refinements with procedure needs to be made for synthesizing Mn NP

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