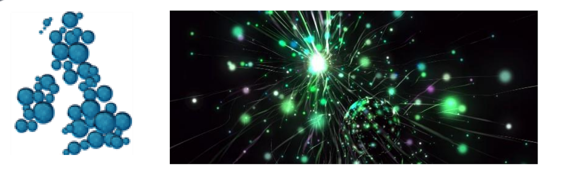
Preparation of Metal Oxide Complexes for Thin Film Fabrication via Aerosol Jet Printing



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Introduction

- Semiconductors are a class of **highly versatile materials**. Uses span across a range of applications including: Photovoltaic Cells, Thin Film Transistors and Light Emitting Diodes

Figure 1. Example of thin film electronics.

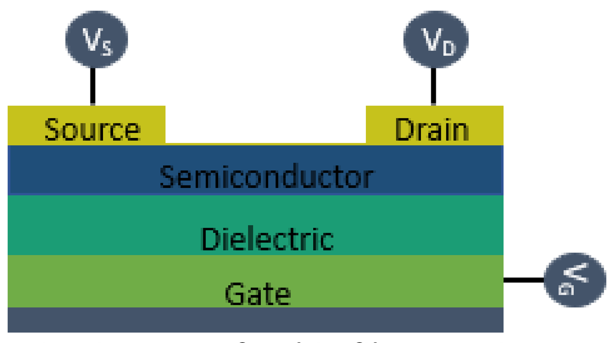


Figure 2. Diagram of a thin film transistor.

- Want **thinner**, **flexible** materials with **higher efficiency** at **lower cost**
- **Metal oxide** and **chalcogenide** semiconducting materials are emerging as a solution
- Current gap in research: high performance **p-type oxide** materials
- **SnO** is a **p-type** semiconductor with a large indirect optical **band gap** of **2.68–2.7 eV**
- **Mobility** has been reported at 1.3 $cm^2V^{-1}S^{-1}$ [1]
- Will look at range of semiconducting metal oxides, initially **SnO** then **VO_2**, **TiO_2** as well as mixed metal systems in the form **$MSnO_2$** where **M** is **Li**, **Na** or **K**

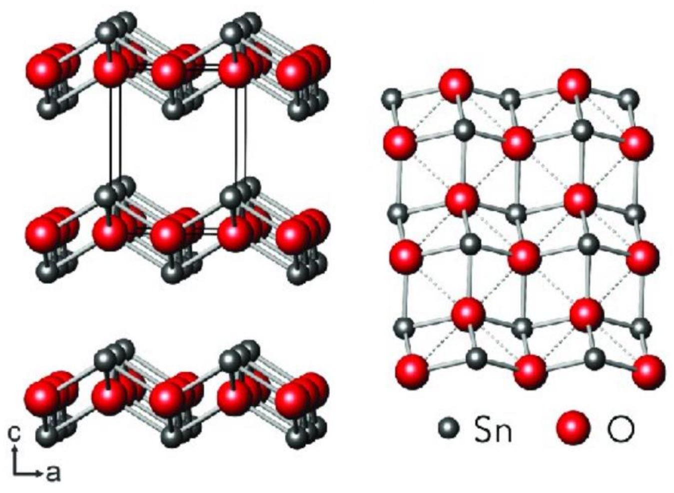


Figure 3. Solid state structure of SnO. [2]

Aerosol Jet Printing

- Aerosol Jet Printing (**AJP**) has recently attracted the interest of the **electronics industry** as an alternative to established thin film fabrication methods such as CVD
- Deposition is done via **high resolution printing** of a **functional ink**
- This work involves making **semiconducting precursors** that can be formulated into **inks** and subsequently **deposited** by **AJP**

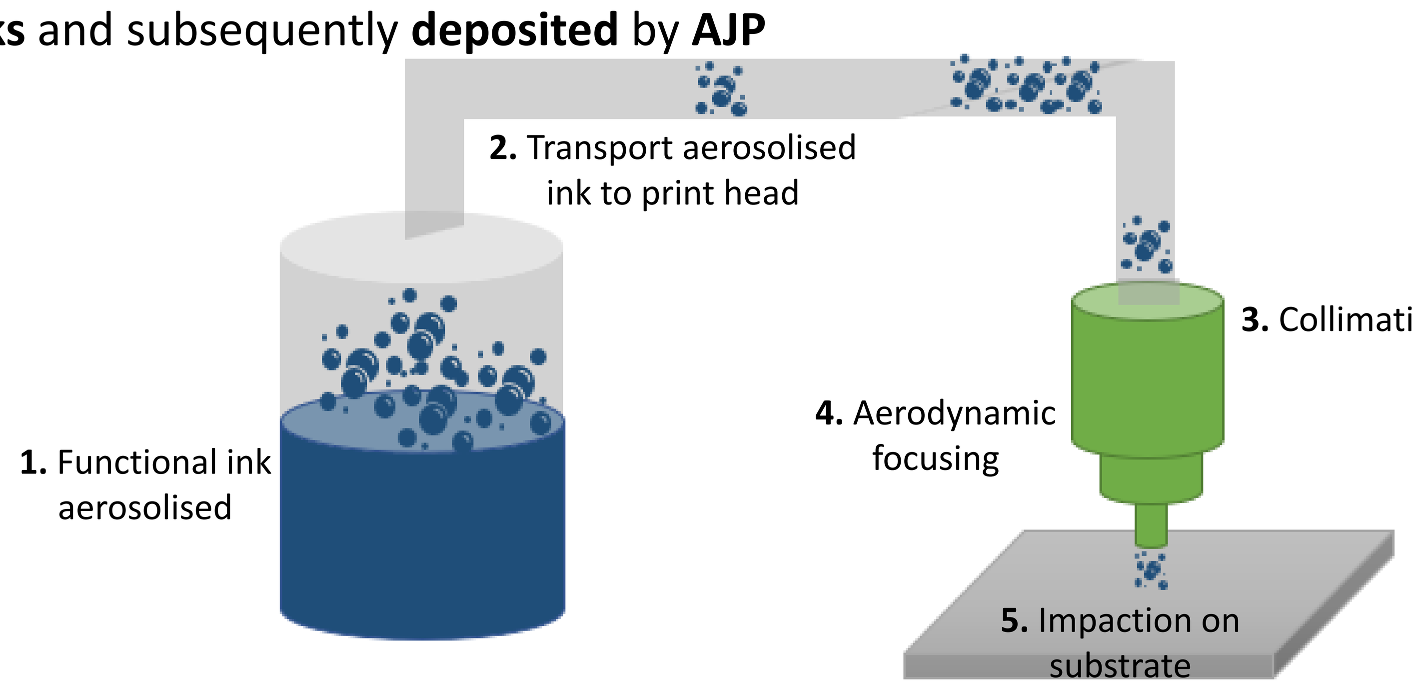
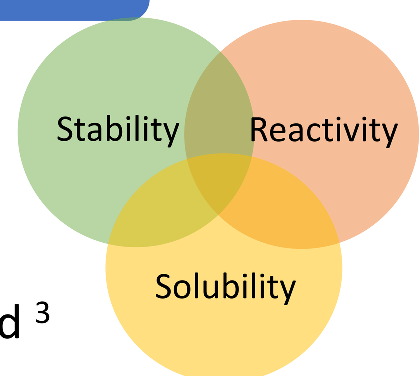


Figure 4. Generalised schematic of the aerosol jet printing process.

- Ink formulation and proof of concept using a Dimatix dmp-2800 ink jet printer

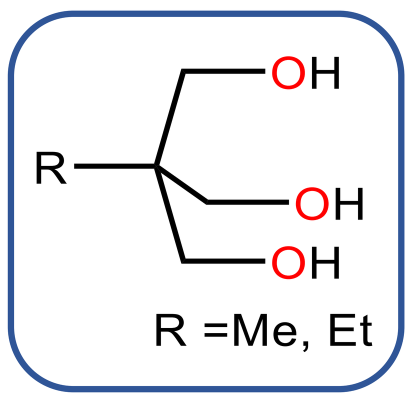
Precursor Requirements

- **Stable** over long time periods within the ink formulation
- Highly **soluble** in organic solvents
- Organic fractions removed at **low temperatures**
- Gives **controlled reactions** with moisture (sol-gel) when deposited [3]

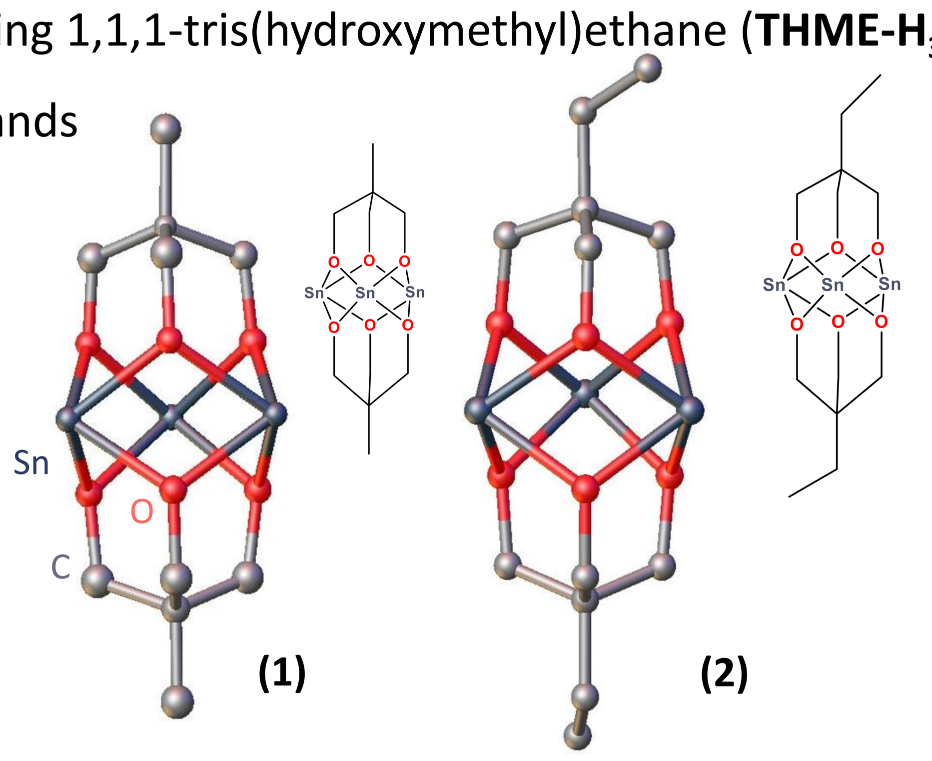


Precursor Development

- A series of **mono-metal systems** were synthesised using 1,1,1-tris(hydroxymethyl)ethane (**THME-H_3**) and 1,1,1-tris(hydroxymethyl)propane (**THMP-H_3**) ligands



$Sn(N(Si(Me_3)_2)_2$ 3:2

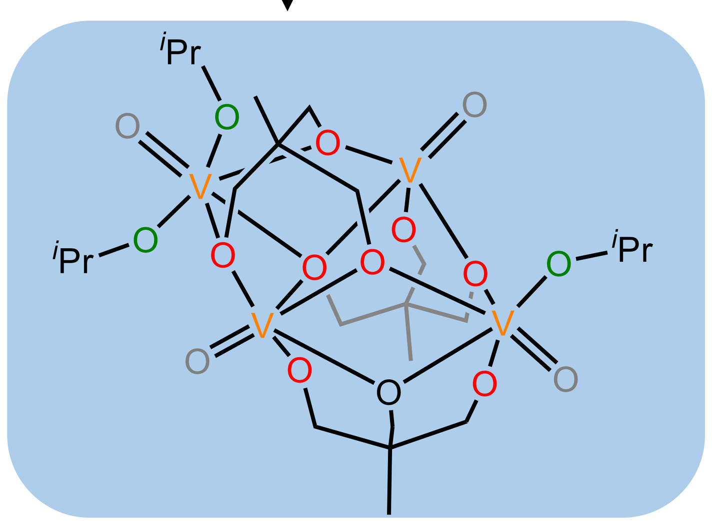


(1) (2)

Figure 5. Molecular structure of $Sn_3(THME)_2$ [4] (1) and $Sn_3(THMP)_2$ (2).

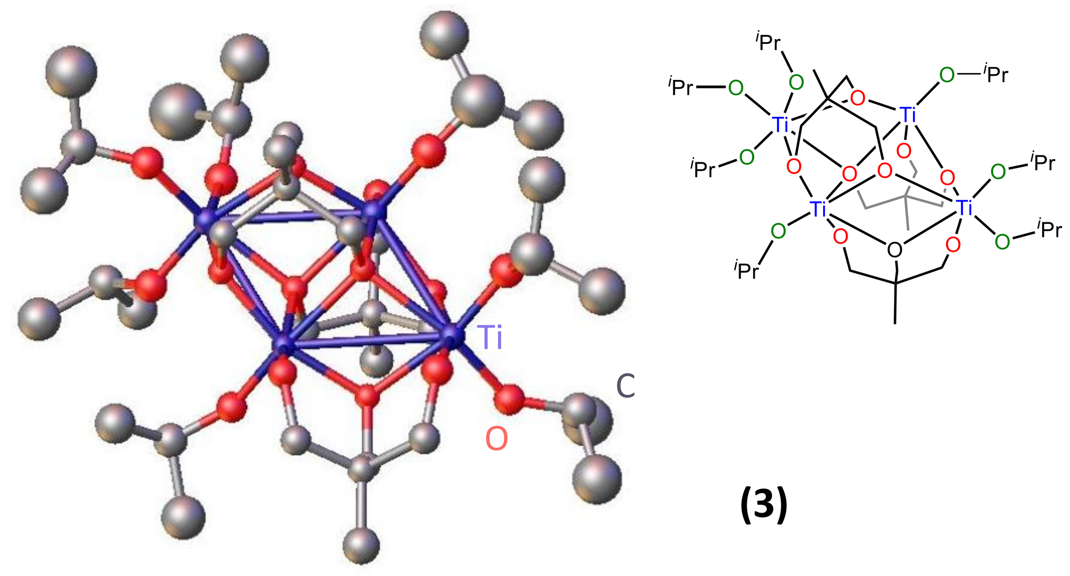
$OV(O^iPr)_3$ 4:3

$Ti(O^iPr)_4$ 4:3



(4)

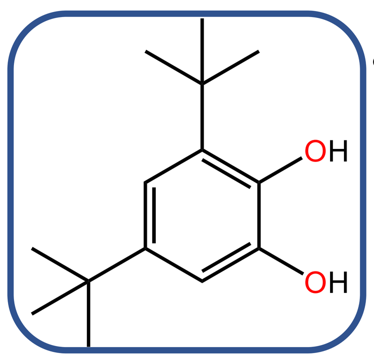
Figure 6. Structure of $V_4(O)_4((THME)_3(O^iPr)_3$ (4), currently undergoing full data collection.



(3)

Figure 7. Molecular structure of $Ti_4(THME)_3(O^iPr)_7$ (3).

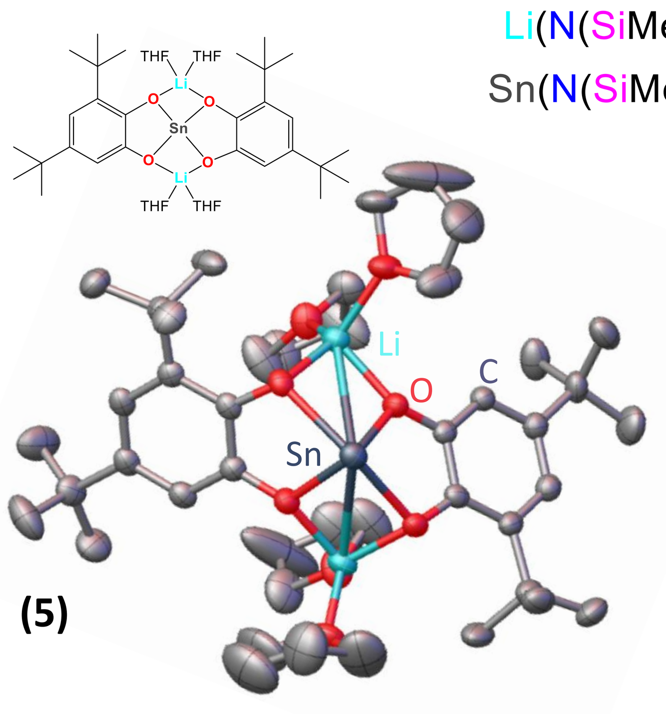
- A series of **mixed metal systems** were synthesised using **catechol ligands,** all with **Sn** centres and either **Li, Na** or **K** in the structure
- Compounds **6** and **7** are **dimers**
- **6** is a **Sn(IV)** complex, the Sn(II) analogue was unable to be attained



$Li(N(SiMe_3)_2)$, $Sn(N(SiMe_3)_2)_2$

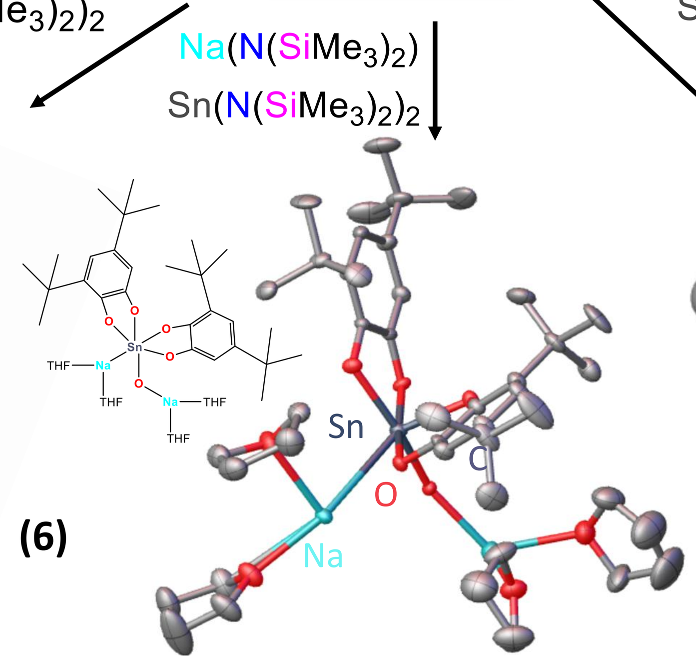
$Na(N(SiMe_3)_2)$, $Sn(N(SiMe_3)_2)_2$

$K(N(SiMe_3)_2)$, $Sn(N(SiMe_3)_2)_2$



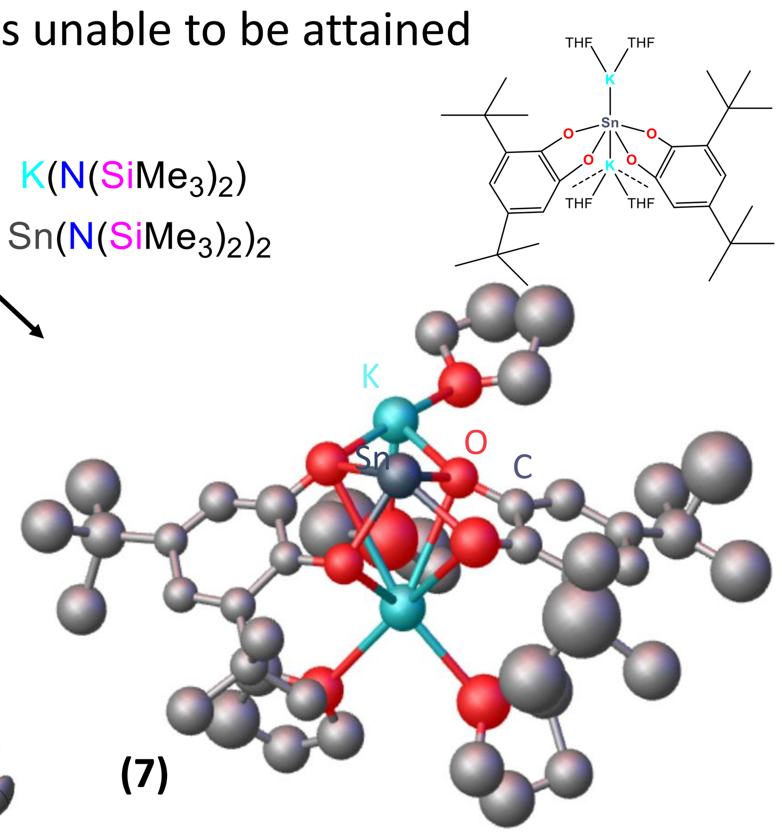
(5)

Figure 8. Molecular structure of $Sn(Li)_2(C_6H_2O_2(^tBu)_2)_2(THF)_4$ (5).



(6)

Figure 9. Molecular structure of $SnO(Na)_2(C_6H_2O_2(^tBu)_2)_2(THF)_4$ (6).



(7)

Figure 10. Molecular structure of $Sn(K)_2(C_6H_2O_2(^tBu)_2)_2(THF)_4$ (7).

Thermal and Volatility Studies

- **Thermogravimetric analysis** of **1, 2, 4, 5** and **7** was undertaken

Compound	Onset	Final w%	Expected w% to give desired metal oxide
1	194	4	23
2	207	4	22
4	95	33	32
5	96	33.41	29
7	96	46.08	36

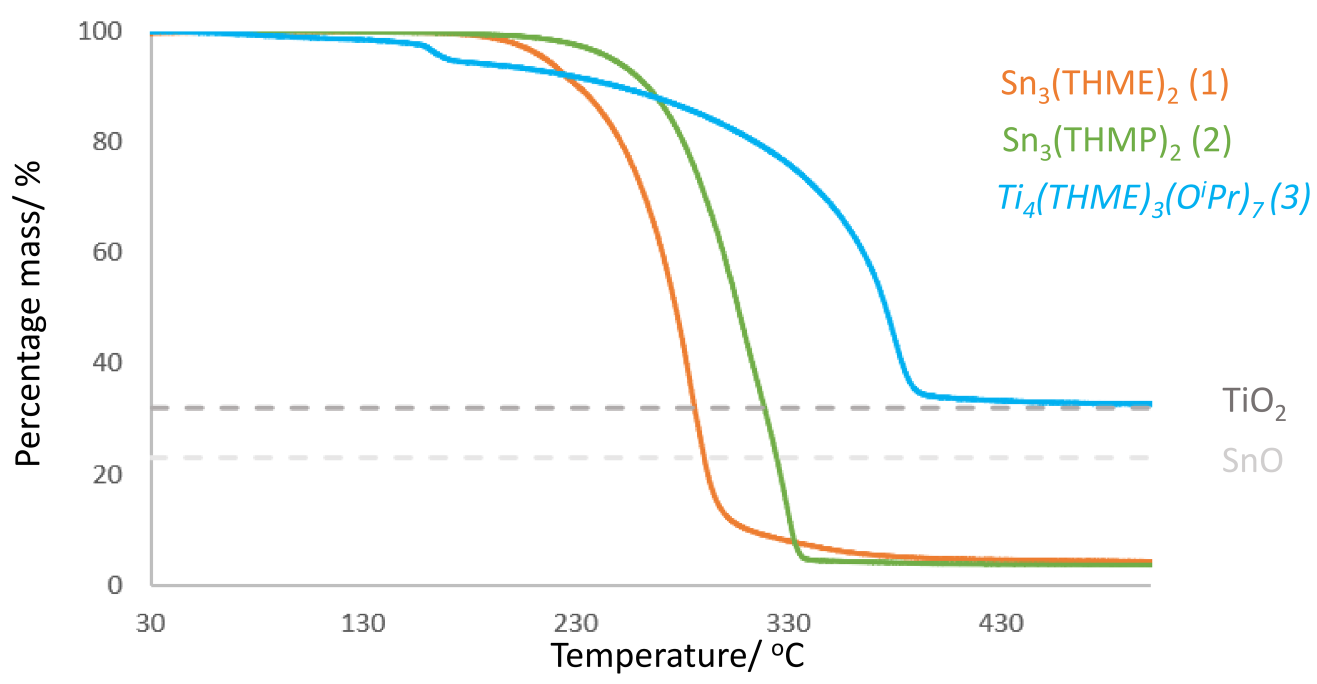


Figure 11. Thermogravimetric analysis plot showing the decomposition of the mono metal systems. $Sn_3(THME)_2$, $Sn_3(THMP)_2$ and $Ti_4(THME)_3(O^iPr)_7$.

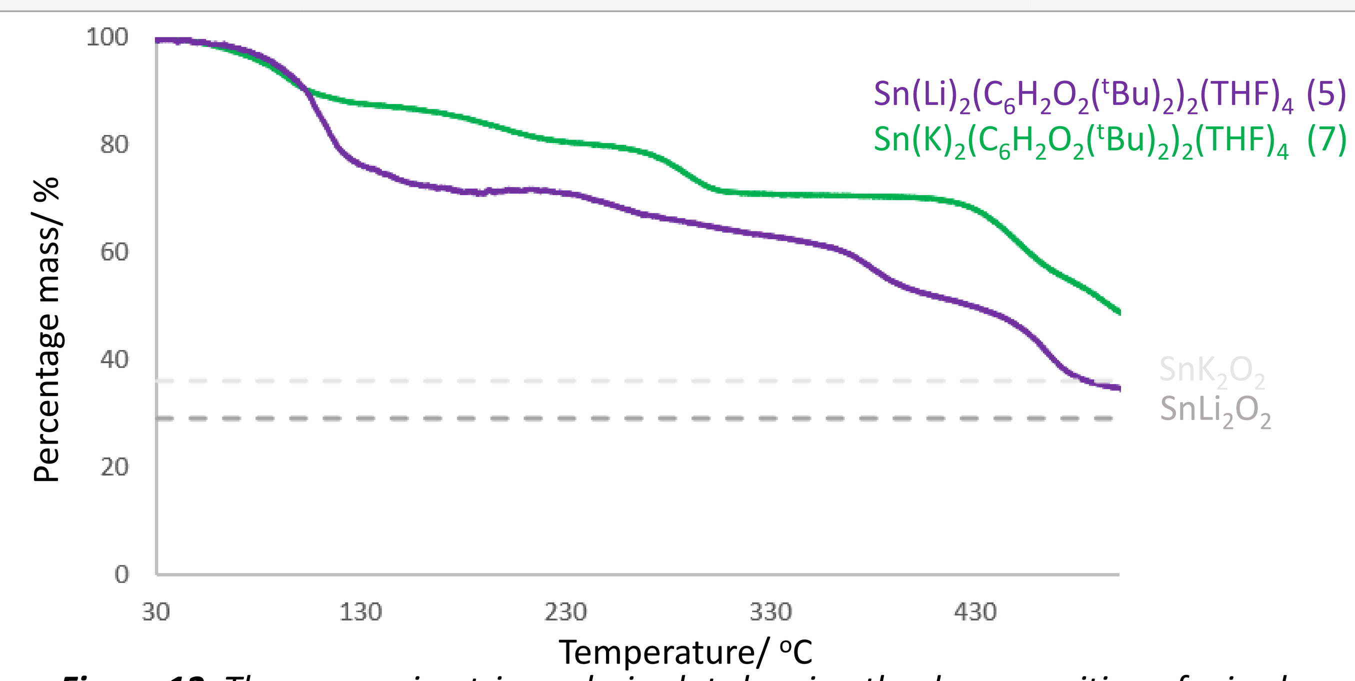


Figure 12. Thermogravimetric analysis plot showing the decomposition of mixed metal systems, $Sn(Li)_2(C_6H_2O_2(^tBu)_2)_2(THF)_4$ and $Sn(K)_2(C_6H_2O_2(^tBu)_2)_2(THF)_4$.

Conclusion and Future Work

- A **series of metal alkoxides** using **THME-H_3** and **THMP-H_3** were successfully synthesised and characterised, along with a **series of alkali metal tin catechol complexes**
- Need to get **full characterisation** data for the **vanadium structure**
- Look at **widening the scope** of the complexes with these ligands
- Next steps involve **formulating** these **precursors** into **inks** and **depositing** using **aerosol jet printing**

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4. T. J. Boyle, J. M. Segall, T. M. Alam, M. A. Rodriguez, J. M. Santana, *J. Am. Chem. Soc.*, 2002, **124**, 6904 – 6913.