Synthesis, characterization and spectral studies of copper, lead and tin dithiocarbamate complexes: Single source precursors for preparation of metal sulphide nanoparticles.

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Outline

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- Introduction
- Methodology
  - *Synthesis*
  - *Characterization*
- Results
  - *FTIR and **Un-Vis***
  - *NMR*
  - *TGA and PL*
  - *SEM and HRTEM*

  Conclusions

  References
- Acknowledgements

Introduction

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The energy situation

The geometric political constrains

Moreover, generic use of fossil fuels

Renewable energy

Solar energy

PV market

Introduction

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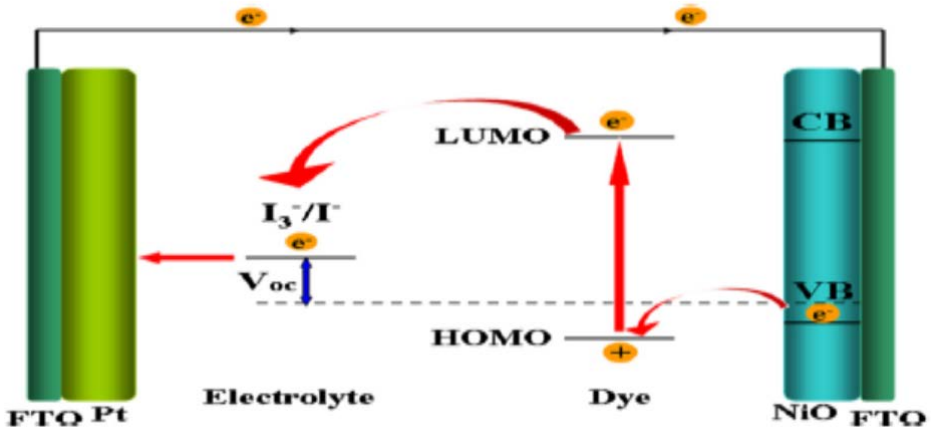
TECHNOLOGY	CAPITAL COSTS USD / kW	ENERGY COSTS US cents / kWh1
POWER GENERATION		
Bio-power from solid biomass (including co-firing and organic MSW)	800–4,500 (Global) Co-fire: 200–800 (Global)	3–22 (Global) Co-fire: 4–12 (Global)
Bio-power from gasification	2,050–5,500 (Global)	6–24 (Global)
Coal (Fossil Fuel)	Coal: 500–6,500	Coal: 5–7
Geothermal power	Condensing flash: 1,900–3800	Condensing flash: 4–14
Hydropower: Grid-based	Projects ≥20 MW: 750–2,500	Projects >20 MW: 2–8
Ocean power: Tidal range	5,290–5,870 (Global)	21–28 (Global)
Solar PV: Rooftop	Residential costs: 2,200 Commercial costs: 3,800	21–44 (OECD)
Solar PV: Ground-mounted utility-scale	1,200–3,000 (Global)	11 (United States)
Concentrating solar thermal power (CSP)	Trough 6,000–8,000 Tower: 6,000 9,000	17–37 (6 hours storage Tower: 12.5–16.4 (United States; high end of range is with storage)

Introduction



- low volatility and high viscosity of electrolytes.
- non-optimized dark current.
- poor contact between the electrolytes.
- poor performance of dye on the NIR region.
- low spectral response.

This study focuses on synthesis of single source precursors of dithiocarbamate complexes of PbS, CuS and SnS QDs.

Methodology

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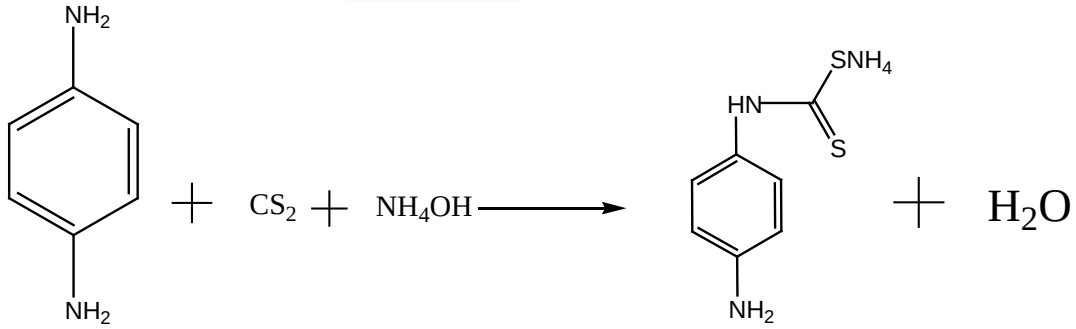
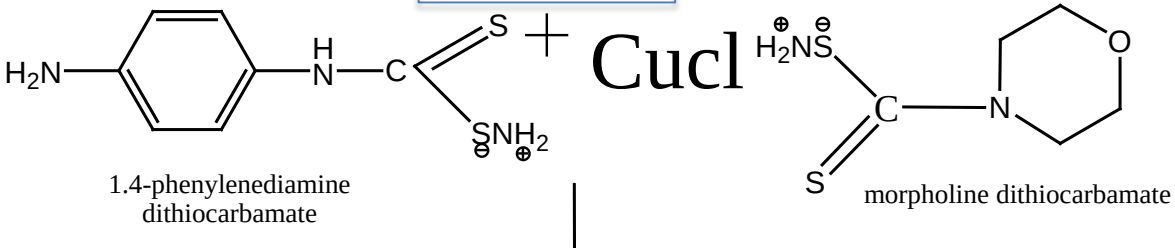
Ligand



1.4 phenylenediamine

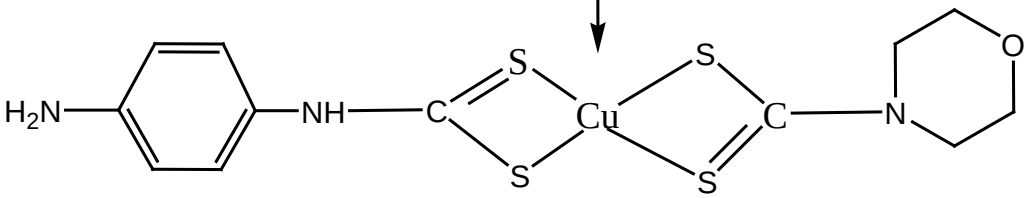
1.4 phenylenediamine dithiocarbamate

Complexes



1.4-phenylenediamine dithiocarbamate

morpholine dithiocarbamate



Results: FTIR Analysis

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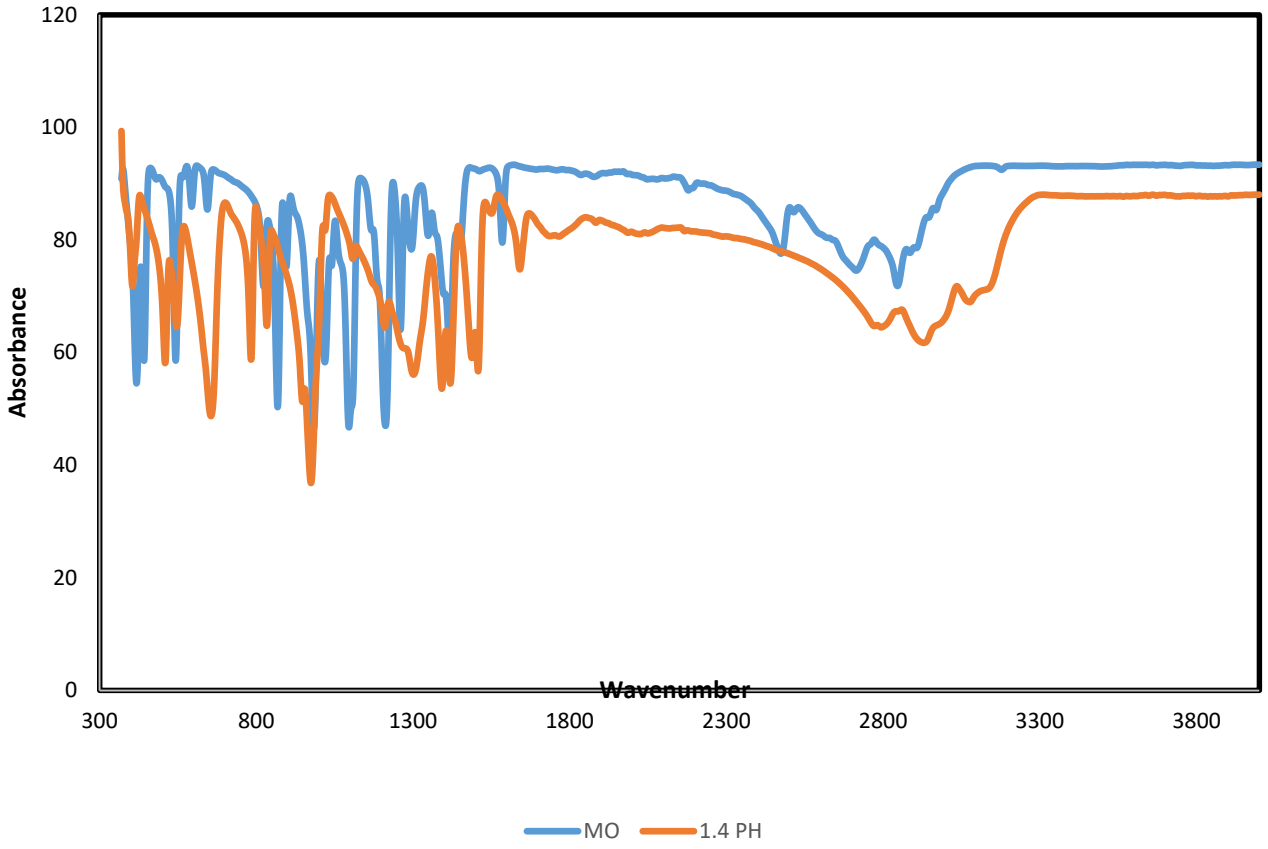
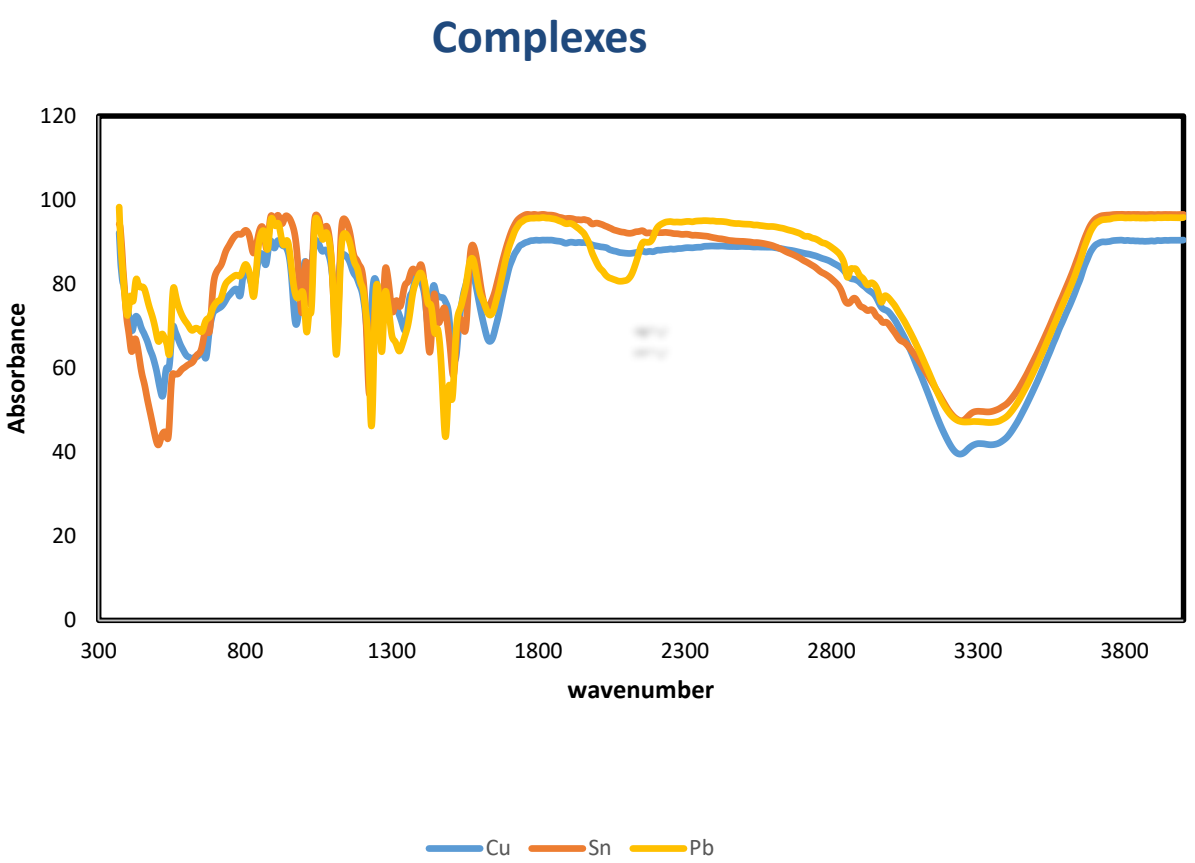
Ligands



- FTIR
- n(C-N) 1507 - 1584 has revealed the thiouride band.
- n(C-S) 974 - 983 indicates that this ligands acted as bidentate chelating type.

Results: FTIR Analysis



- FTIR
- n(C-N) 1503 - 1513 revealed the thiouride band.
- n(M-S) 416 - 625 for metals band.
- n(C-S) 973 - 1030 indicates that this ligands acted as bidentate chelating type.

Results: NMR Proton Analysis

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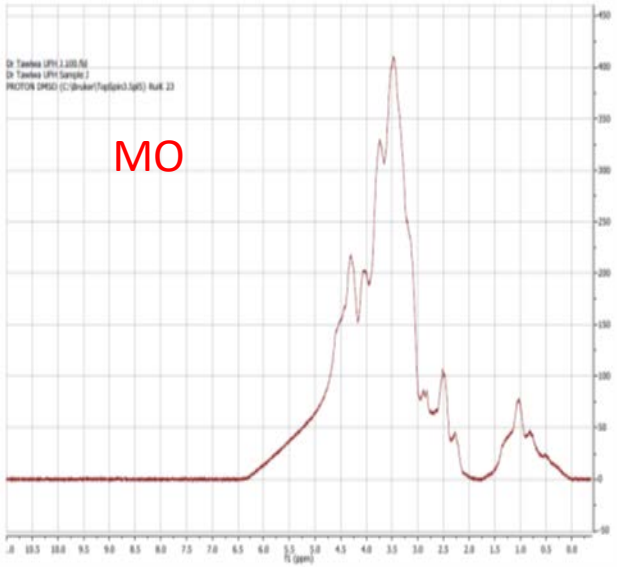
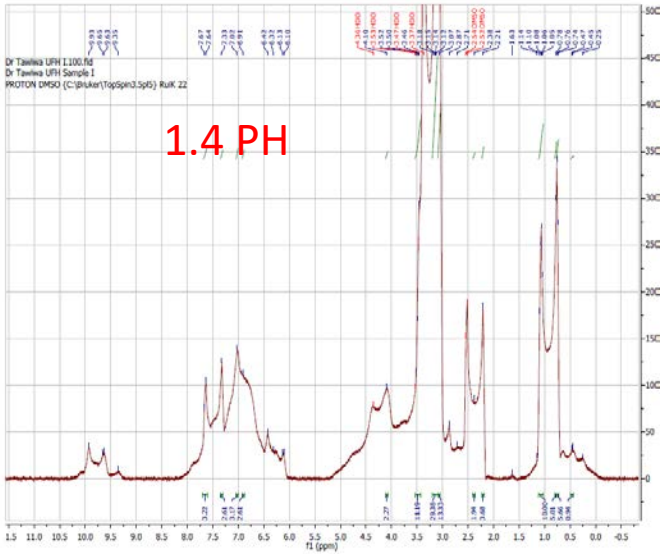
Ligands





- ^{1}H NMR spectra of the ligands revealed signals of 2.8 - 4.3 ppm for $CH_{2,}$ RNH_{2} at 9.3 – 9.9 ppm, and the solvents at 2.5 ppm, which corresponds to the protons of the ligands of DTC.

- While the signal of 6.10 - 7.6 ppm for the phenyl ring which is in line with protons of DTC.

Results: NMR Proton Analysis

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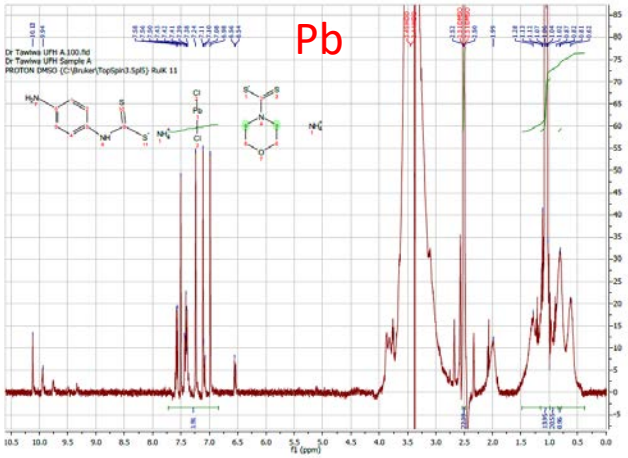
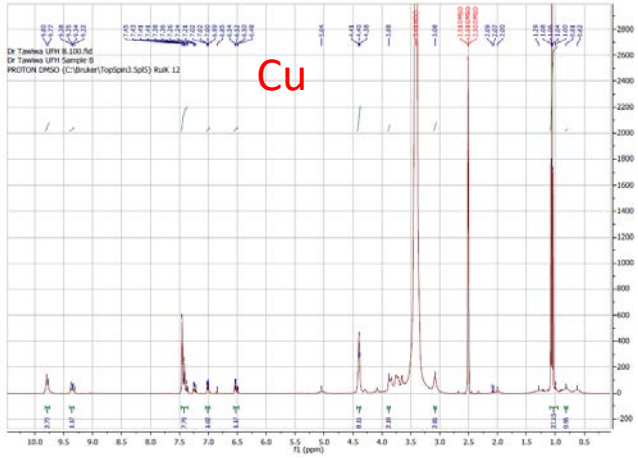
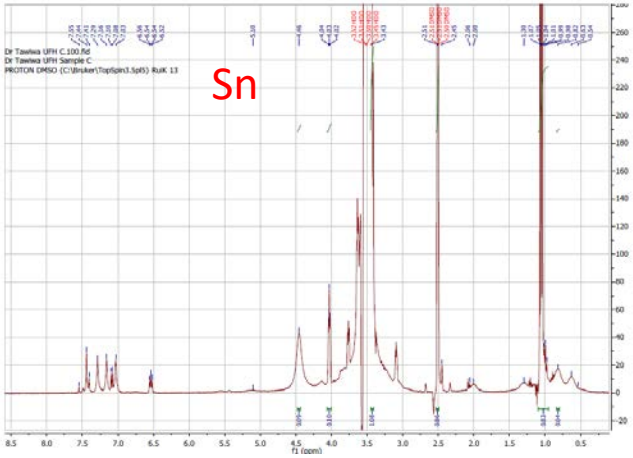
Complexes







- ^{1}H NMR spectra of the ligands revealed signals of 3.4 – 5.10 ppm for CH_2, RNH_2 at 7.03 – 10.12 ppm, and the solvents at 2.5 ppm, which corresponds to the protons of the ligands of DTC.

- While the signal of 6.48 - 7.58 ppm for the phenyl ring which is in line with protons of DTC.

Results: NMR Carbon Analysis

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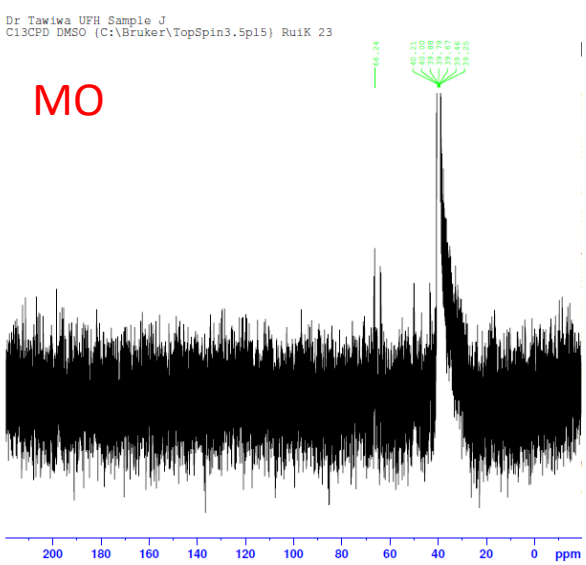
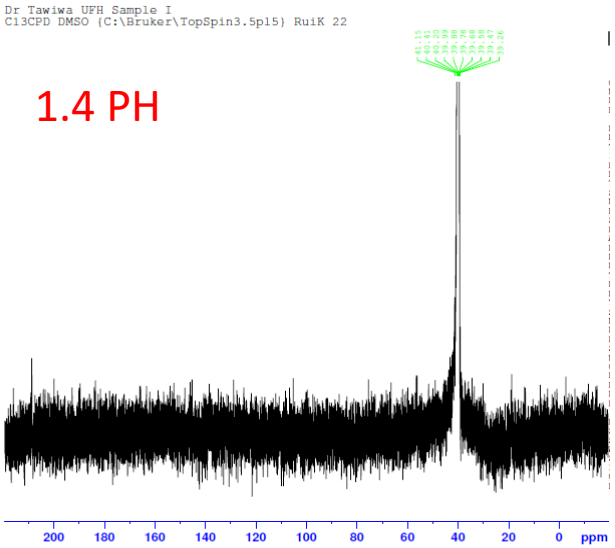
Ligands





- ^{13}C NMR spectra, for the DTC ligands. The signal around 39.25 – 39.99 ppm is due to CH2; while the signal with higher intensity was observed at 40 ppm for the NH2.

- The signal at 195 – 208 ppm is due to CS2.

Results: NMR Carbon Analysis

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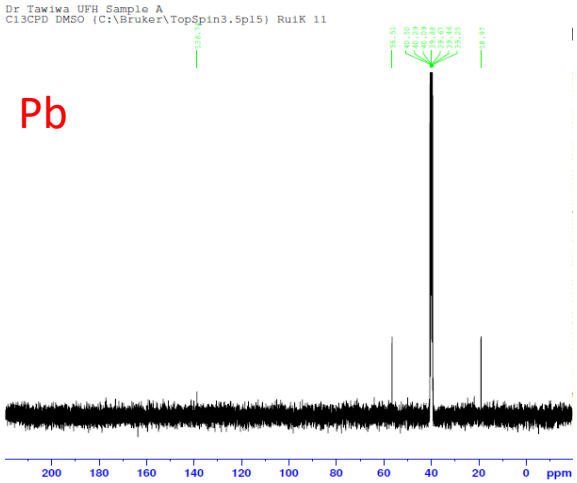
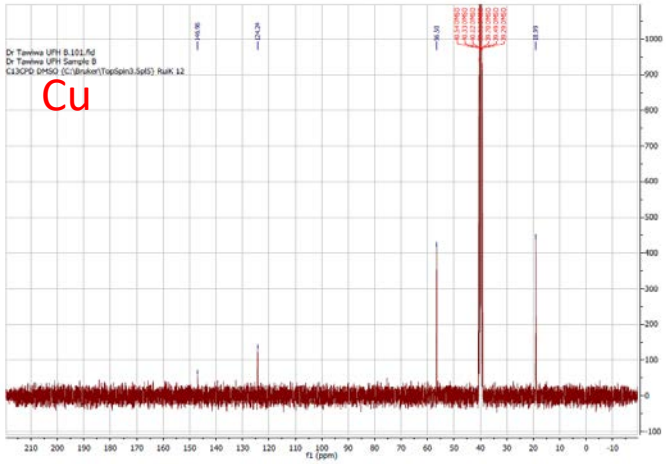
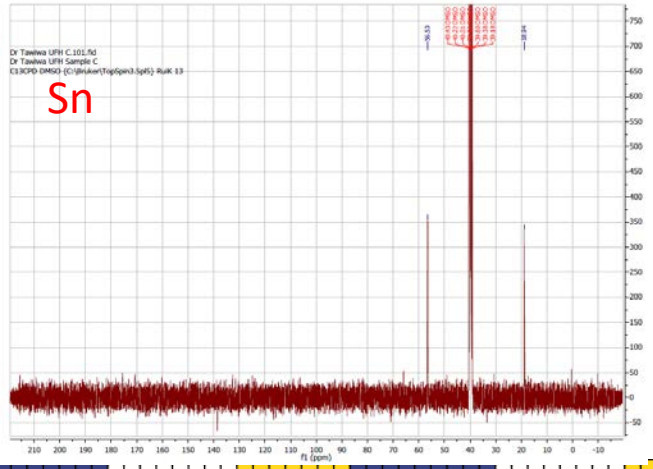
Complexes



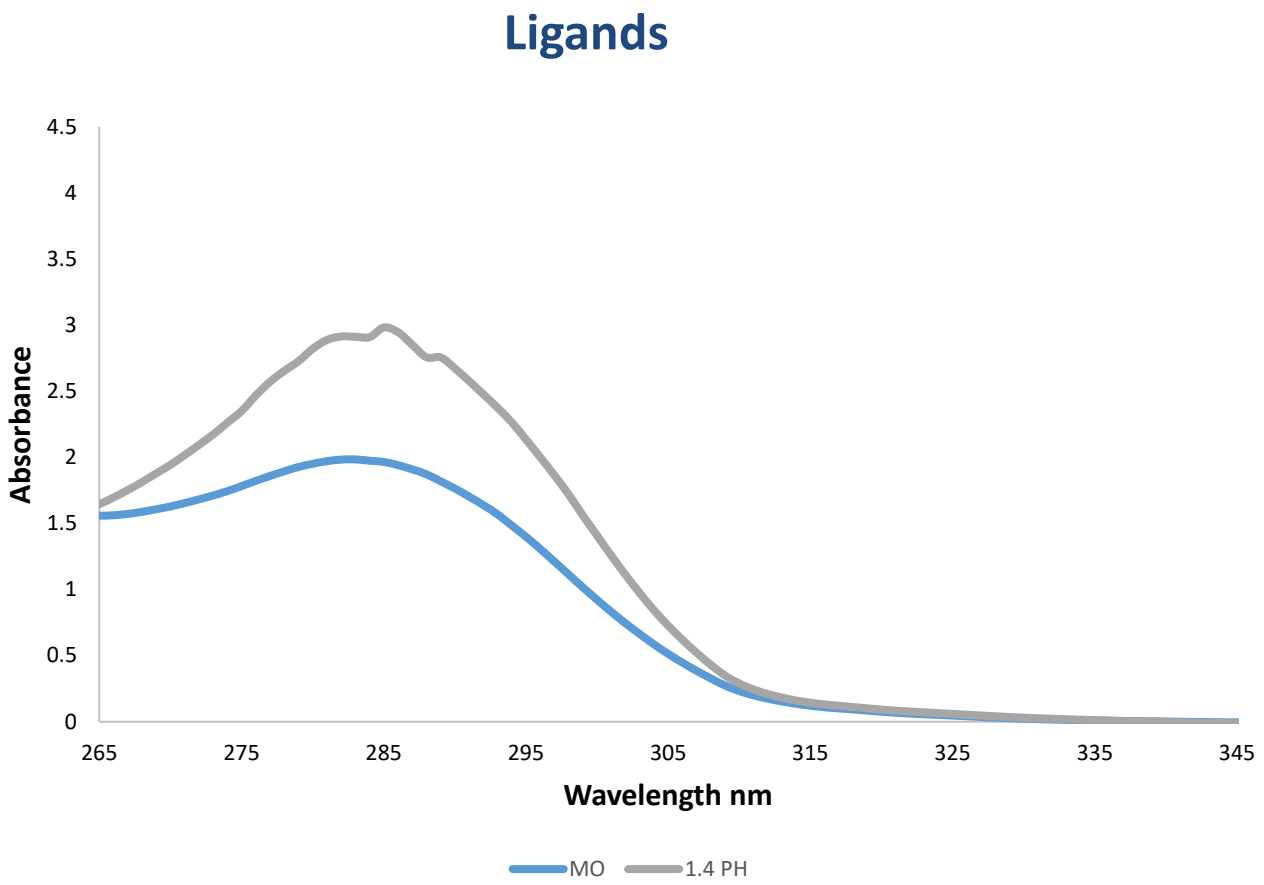




- ^{13}C NMR spectra, for the DTC complexes. The signal around 18 – 56 ppm is due to CH2; while the signal with higher intensity was observed at 40 ppm for the NH2.

- The signal at 124 – 148 ppm is due to phenyl rings.

Results: UV-Vis



The electronic spectra of DTC ligands revealed a band at 286 nm for both ligands as a results of intraligand $\pi \rightarrow \pi^*$ transitions located on the N–C=S group, $\pi \rightarrow \pi^*$ transition within the S–C=S group and $n \rightarrow \pi^*$ electronic transition located on the sulphur atom lone pair electron. The effect of conjugate on 1.4 PH DTC can be ascribed to the difference between the two ligands.

Results: UV-Vis

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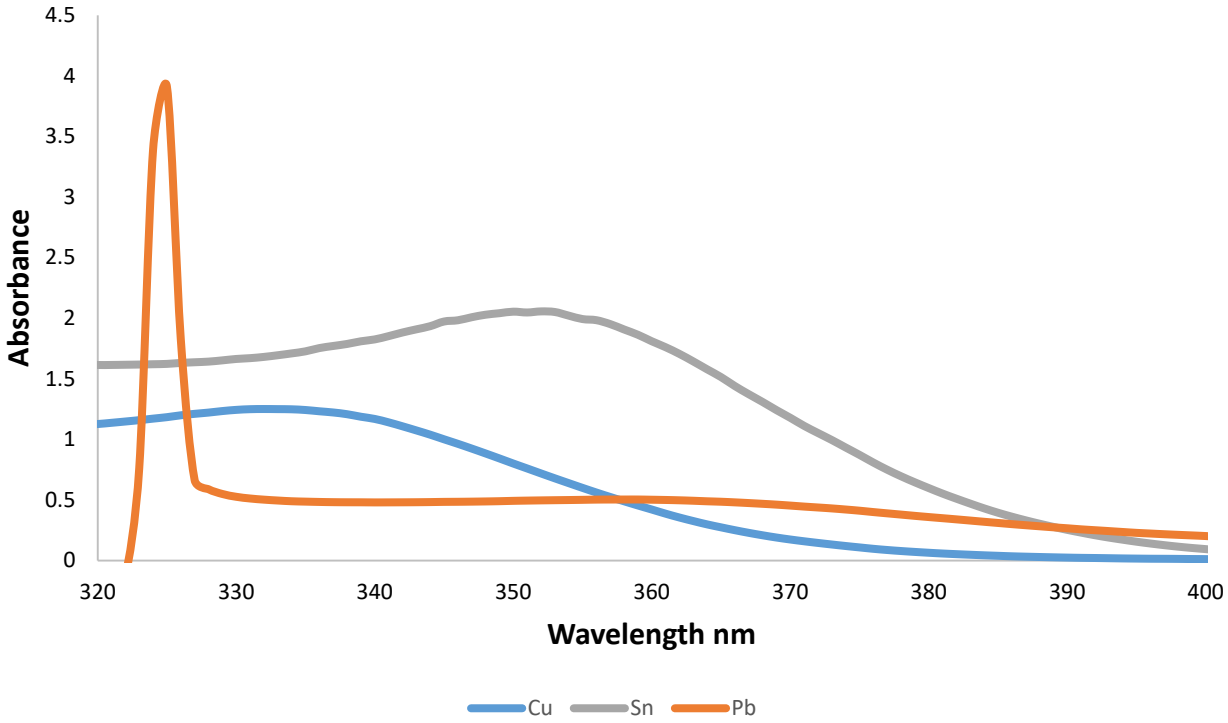
Complexes



The electronic spectra of DTC complexes revealed a band at 325 nm for Pb, 338 nm for Cu and 356 nm for Sn as a results of intraligand $\pi \rightarrow \pi^*$ transitions located on the N–C=S group, $\pi \rightarrow \pi^*$ transition within the S–C=S group.

Results: PL

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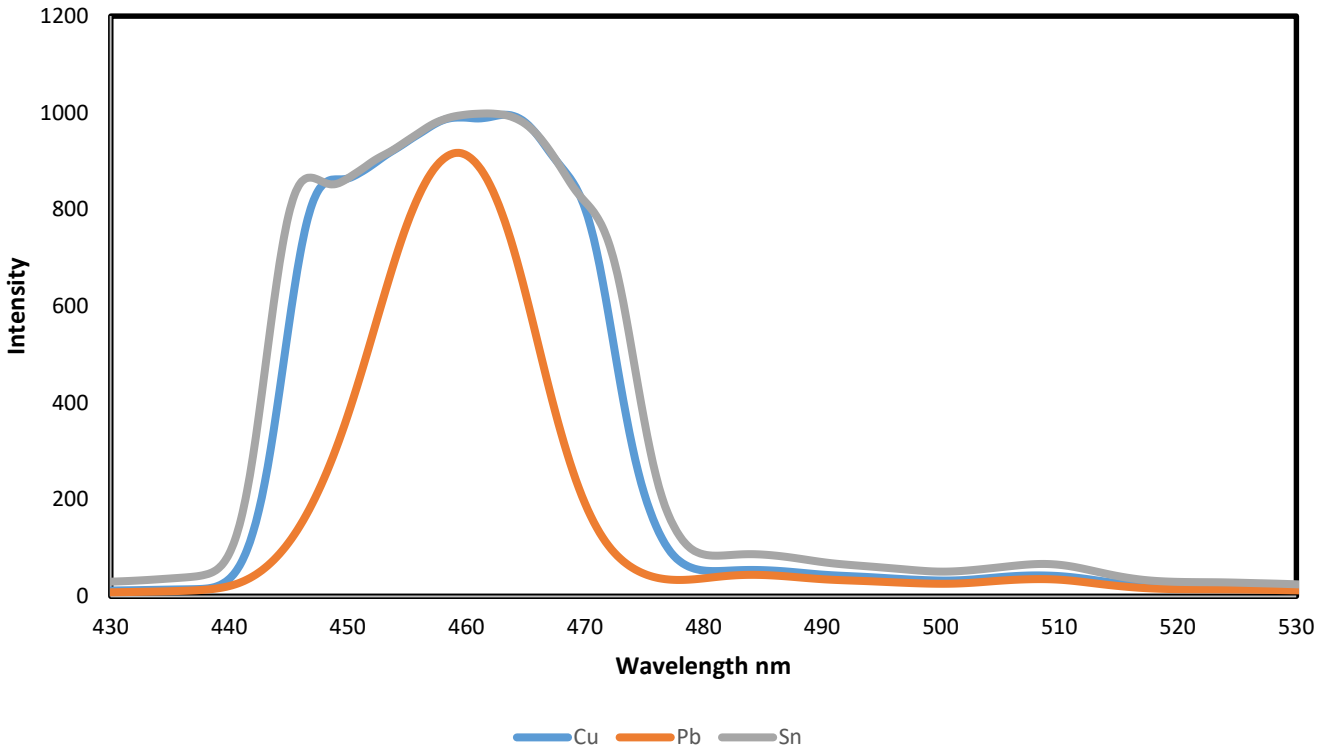
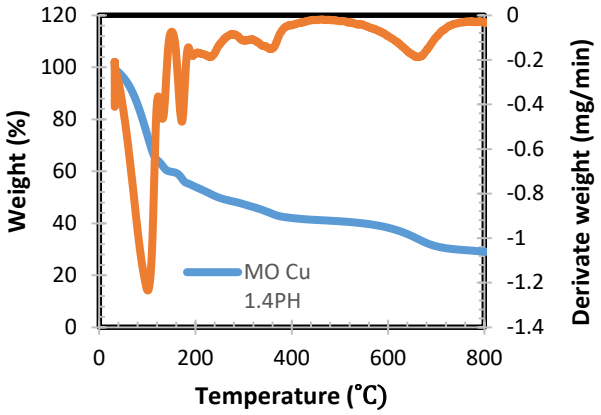
Complexes

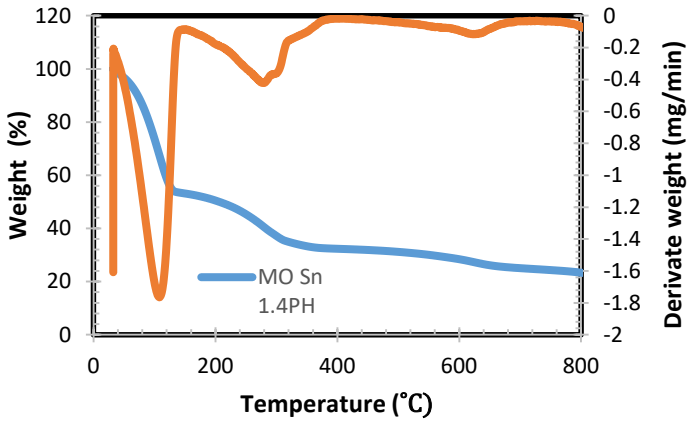


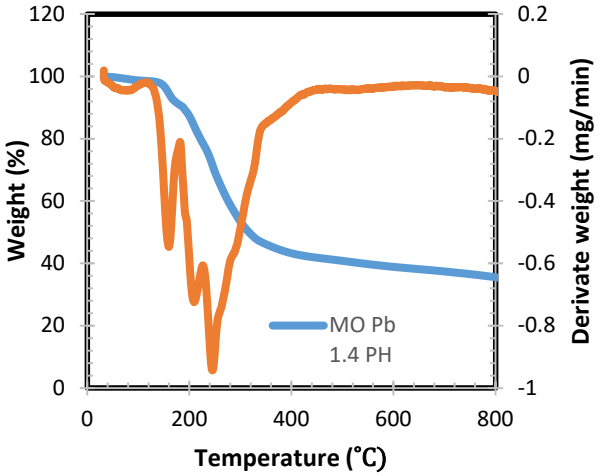
The electronic spectra of DTC complexes revealed a broad and sharp peaks at 460 nm for Pb and 462 nm for both Cu and Sn.

They are all in the Blue-shift region.

Results: TGA







The TGA revealed spectra of three steps from 150 °C, 377 °C and 729 °C for Cu with a mass residue of 30 % CuS.

Sn also has three steps from 123 °C, 321 °C and 656 °C with mass residue of 25% SnS.

While Pb has two steps at 170 °C and 360 °C with mass residue of 36% PbS.

Results: SEM

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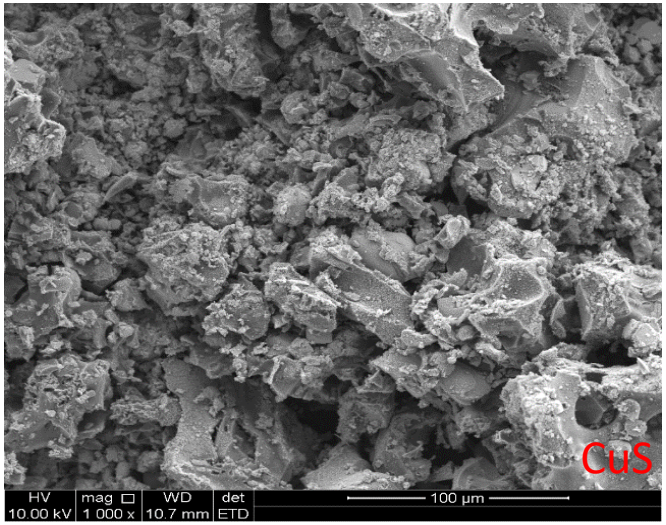

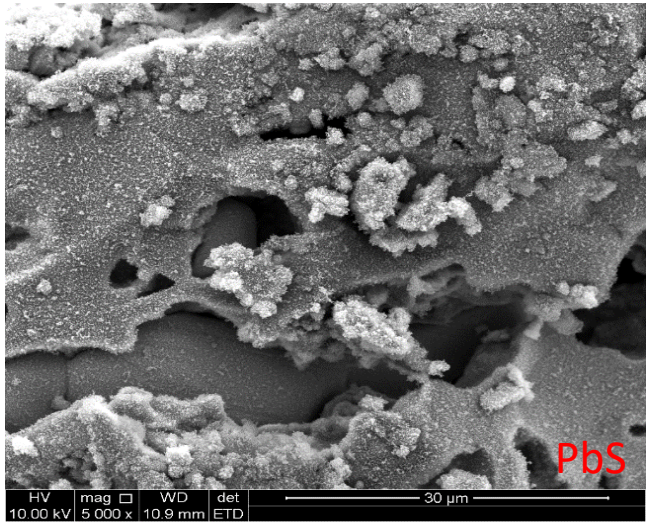

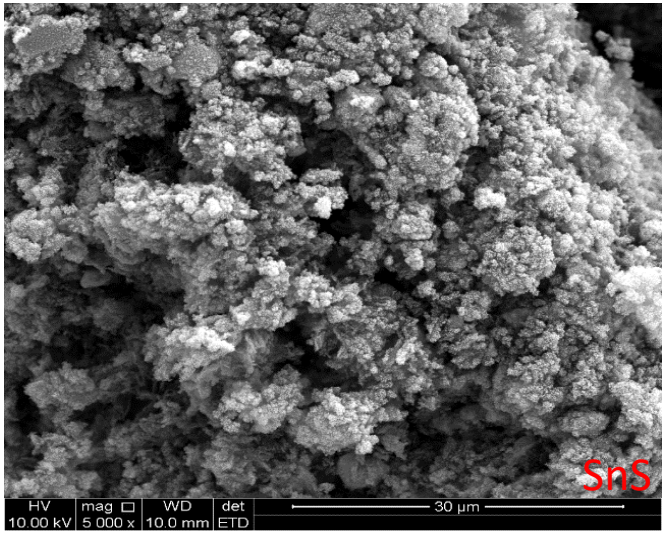

The SEM results revealed spherical shape, some crystalline and cubic structure for the CuS.

PbS shows a large spherical with smooth surface and solid morphology, it has a decent development of crystals which show crystallinity spheres.

SnS has a smooth surface comprising of mesoporous nanostructure with small spherical nanoparticles due to agglomeration.

Results: HRTEM

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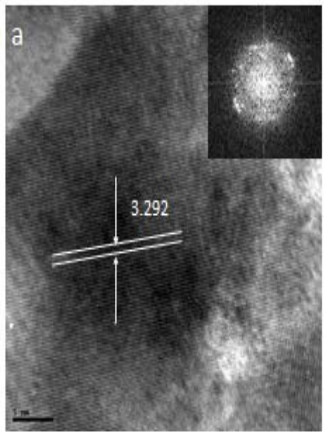
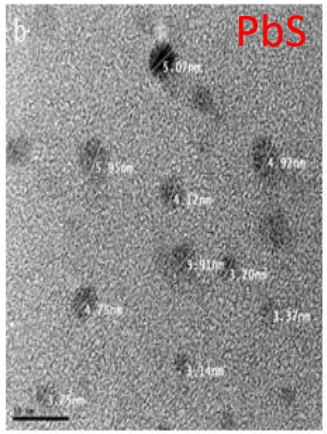
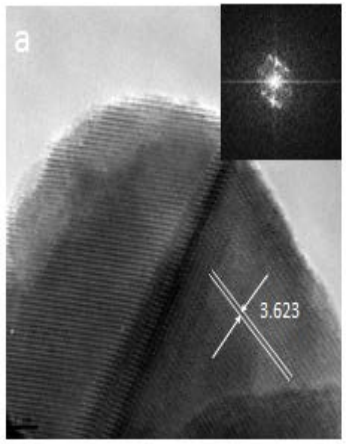
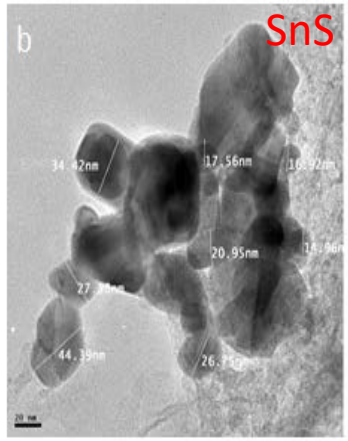
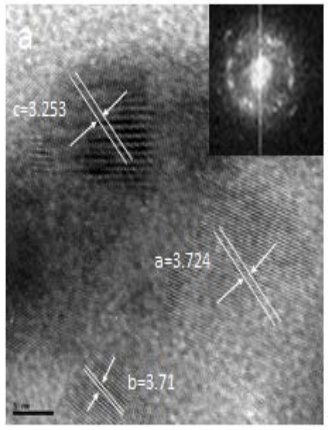


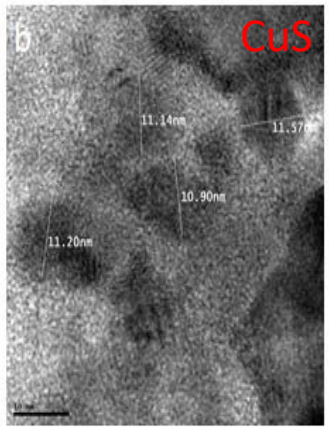






The HRTEM images revealed a spherical shape and polycrystalline in the three samples.





Conclusion

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- FTIR results have shows that the dithiocarbamate complexes and ligands are bidentate.
- The NMR results for proton and carbon confirm the present of DTC in both ligands and complexes, this correlate with the results of the IR.
- TGA decomposition of the complexes were obtain as single source precursors from the residue, which revealed a mass weight within the range of 25-30 % for the metals sulfides.
- SEM analysis has revealed a spherical nanoparticles for the metal sulfides.
- HRTEM images have revealed spherical and polycrystalline nanoparticles.
- PL analysis for the metal complexes has confirmed the presence of absorption, which is within the blue-shift region.

Acknowledgements

- God for honouring is words in Psalm 32:8.
- My supervisors.
- Department of Chemistry and Fort Hare Institute of Technology (FHIT) for giving me an opportunity to utilize their laboratory facilities.
- Acknowledging the support of :

THANK YOU ALL