On the Synthesis, Properties, and Applications of Metal Dithiocarbamate Complexes

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by

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Certificate of Original Authorship

I, Alexander Angeloski declare that this thesis by publication, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mathematical and Physical Sciences at the University of Technology Sydney.

This thesis by publication is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Publications arising from this work

1. A. Angeloski, A.T. Baker, M. Bhadbhade, A.M. McDonagh, "Bis(κ^2S,S'-di(isopropyl)dithiocarbamato)nickel(II): Anagostic C-H···Ni interactions and physical properties", *Journal of Molecular Structure*, 2016, 1113, 127-132
2. A. Angeloski, J.M. Hook, M. Bhadbhade, A.T. Baker, A.M. McDonagh, "Intramolecular H···S interactions in metal di(isopropyl) dithiocarbamate complexes", *CrystEngComm*, 2016, 18, 7070-7077
3. A. Angeloski, A.R. Gentle, J.A. Scott, M.B. Cortie, J.M. Hook, M.T. Westerhausen, M. Bhadbhade, A.T. Baker, A.M. McDonagh, "From Lead(II) Dithiocarbamate Precursors to a Fast Response PbS Positive Temperature Coefficient Thermistor", *Inorganic Chemistry*, 2018, 57, 2132-2140
4. J.A. Scott, A. Angeloski, I. Aharonovich, C.J. Lobo, A.M. McDonagh, M. Toth, "In situ study of the precursor conversion reactions during solventless synthesis of Co_9S_8, Ni_3S_2, Co and Ni nanowires", *Nanoscale*, 2018, 10, 15669-15676
5. A. Angeloski, M.B. Cortie, J.A. Scott, D.M. Bordin, A.M. McDonagh, "Conversion of single-crystals of a nickel(II) dithiocarbamate complex to nickel sulfide crystals", *Inorganica Chimica Acta*, 2019, 487, 228-233
6. A. Angeloski, A. Rawal, M. Bhadbhade, J.M. Hook, R.W. Schurko, A.M. McDonagh, "An Unusual Mercury(II) Diisopropyldithiocarbamate Coordination Polymer", *Crystal Growth and Design,* 2019, 19, 1125-1133

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Abstract

Metal dithiocarbamate complexes possess many interesting and useful properties which has made them ubiquitous in the literature. Their discovery was early in the field of sulfur chemistry, with their applications as vulcanisation accelerators and fungicides being explored not long after. Nowadays, most published reports focus on their molecular structures, and their use as single source precursors to metal sulfide materials. Much of the research in those fields omits the relationship between their structure and properties, or their mechanism of decomposition to metal sulfide materials. This dissertation presents an investigation into the synthesis of metal dithiocarbamate complexes, with an emphasis on the relationship between their structure and properties, and how these properties affect their use as potential single source precursors to metal sulfide materials. Firstly, investigations into subtle intermolecular interactions were conducted using a nickel(II) dithiocarbamate complex. The complex was subsequently used as a single source precursor to NiS, and provided insight into the mechanisms behind its decomposition. The use of lead(II) dithiocarbamate complexes as precursors to PbS materials was investigated in a study that highlighted the relationship between the structure of the complex, and the resultant PbS material. Along the way, important insights relating to the structure and spectroscopic properties of dithiocarbamate complexes were also gained, leading to an uncovering of the mechanisms behind restricted rotation in di(isopropyl)dithiocarbamate complexes. The dissertation concludes with a study evaluating the mechanisms behind molecular isomerisation in mercury(II) dithiocarbamate complexes.