Complexes of thiophene derivatives as potential metallomesogens

by

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Co-Supervisor: Dr. Marilé Landman

Declaration

I declare that the thesis that I submit for the degree of Doctor of Philosophy in Chemistry at the University of Pretoria has not previously been submitted by me for degree purposes at any other university, and all the sources that were used or quoted have been indicated and acknowledged.

Signature…….. Date……..

Mary Solly Thomas

Contributions of the following collaborators and institutes are acknowledged:

(i) Mr David Liles for data collection, structure determination and discussions regarding the single crystal X-ray diffraction studies

(ii) The Department of Chemistry, Katholieke Universiteit Leuven, Belgium for Polarizing Optical Microscopy (POM) measurements and much needed discussions

(iii) Dr Liezel van der Merwe, University of South Africa (UNISA) for DSC and TGA measurements

(iv) Dr Tommie van der Merwe, University of the Witwatersrand for recording the mass spectra

Summary

Complexes of thiophene derivatives as potential metallomesogens

Candidate:	Mary Solly Thomas
Supervisor:	Prof Simon Lotz
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Department:	Chemistry
Degree:	Doctor of Philosophy

This study involves the synthesis and structural characterization of new metal complexes of thiophene derivatives that have (potential) liquid crystalline properties. Thiophene has been selected because of its stability and versatility in lending itself to synthetic modification and hence forms links in chain structures for rod-like metallomesogens. Thiophene, when compared with 1,4-disubstituted benzene units, can change considerably the polarity, polarizability and also the geometry of the compounds, altering the types of mesophases, phase transition temperatures, dielectric constants and other properties of mesogens.

The reactions of a series of 5-alkyl-2-thiophenedithiocarboxylates with nickel(II) chloride formed two types of complexes, blue mononuclear nickel(II) complexes with two terminal dithiocarboxylate ligands, $[Ni(S_2CTR)_2]$ (T = 2,5-disubstituted thiophene) and violet mononuclear nickel(II) complexes with perthio- and dithiocarboxylate ligands, $[Ni(S_3CTR)(S_2CTR)]$ (R = alkyl groups). The blue monomers are preferred for the shorter alkyl chains (C_4 and C_6), and the violet compounds for the longer chain lengths (C_8, C_{12} and C_{16}) in the alkylthiophene complexes. In addition to the above series, $[Ni(S_2CTCH_3)_2]$, was prepared in a one-pot reaction and it was possible to isolate both the blue and violet products. The

thermal properties of the complexes were studied by using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Nickel complexes of the violet type with longer alkyl chains showed liquid crystalline properties.

Zinc(II) complexes analogous to nickel(II) complexes prepared similarly. A crystal structure determination of one of those complexes revealed the fusion of two monomers to give a dimeric structure with bridging sulfur atoms, $[Zn_2(\mu\text{-}S_2CTR)_2(S_2CTR)_2]$. Although an irregular melting pattern was observed, the complexes did not show any liquid crystalline properties.

In an attempt to extend the study towards organometallic compounds, complexes of the type $[Re(CO)_4(S_2CTR)]$ or $[Re(CO)_4(S_2CTTR)]$ (T = 2,5-disubstituted thiophene, TT = 2,5-disubstituted bithiophene; R = H, CH_3, $C_{14}H_{29}$) were synthesized and characterized by IR and NMR spectroscopy. Further characterization of $[Re(CO)_4(S_2CTTH)]$ by single crystal X-ray diffraction confirmed the molecular structure of the complexes. These compounds showed sharp single melting points.

Fischer-type carbene complexes of manganese(I) with octahedral coordination of the type $[MnMeCp(CO)_2\{C(OEtTR)\}]$ or $[MnMeCp(CO)_2\{C(OEtTTR)\}]$ (R = H, C_6H_{13}, $C_{12}H_{25}$, $C_{16}H_{33}$) were synthesized and characterized by IR, NMR and mass spectrometry. Thermal properties of the complexes were studied by using thermogravimetric analysis (TGA). All the organometallic rhenium(I) and Fischer-type carbene complexes of manganese(I) showed weight loss upon heating due to decomposition. Therefore it can be assumed that these complexes are not suitable as liquid crystals.

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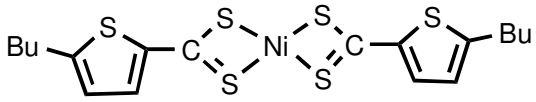
Table of contents

List of Complexes



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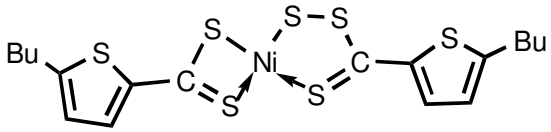

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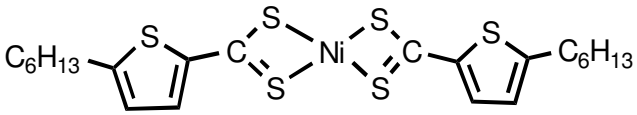

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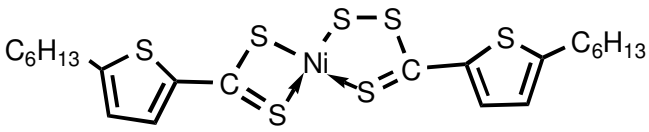

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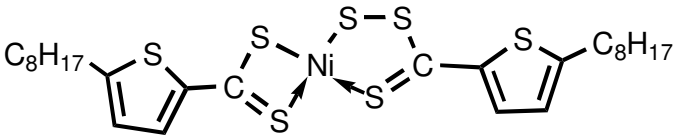

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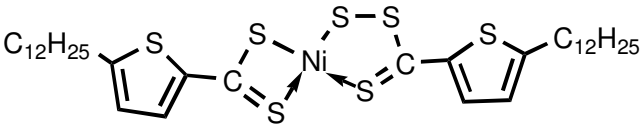

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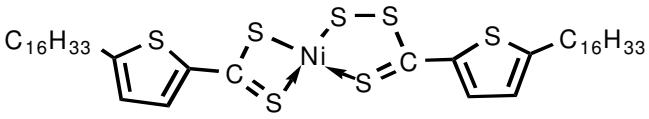

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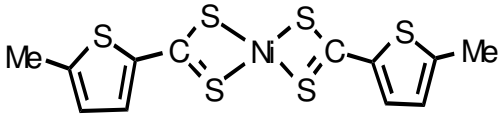

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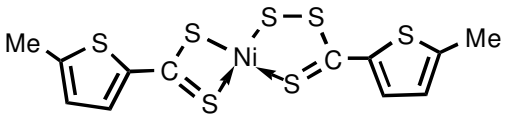

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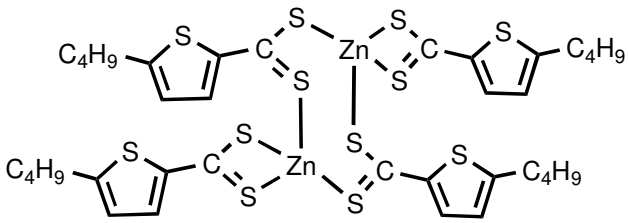

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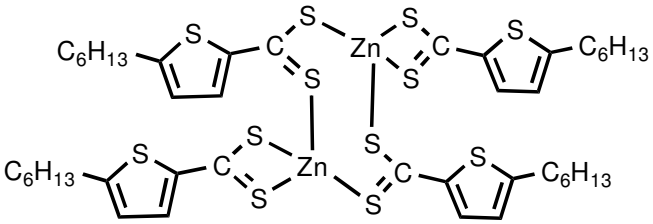

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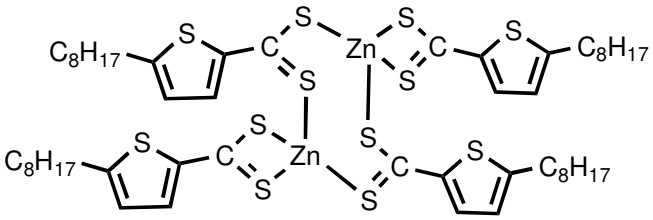

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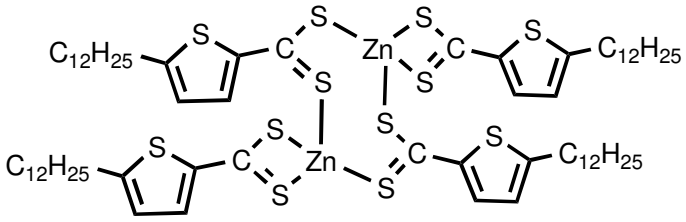

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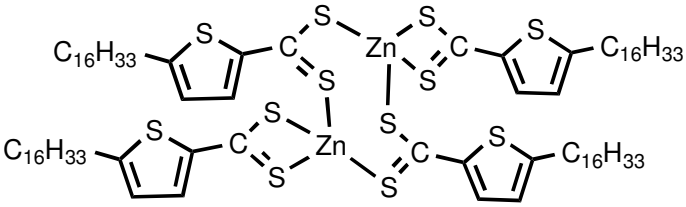

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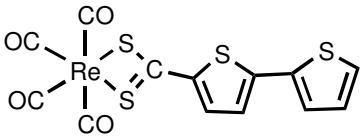

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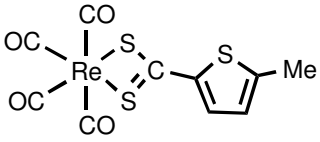

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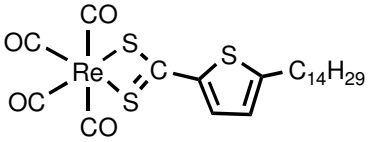

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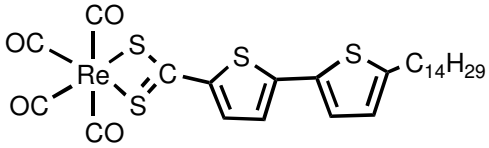

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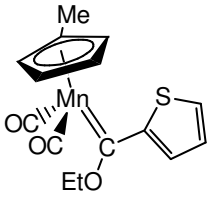

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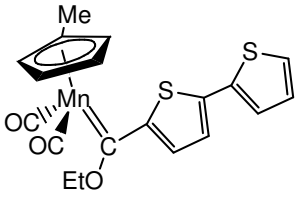

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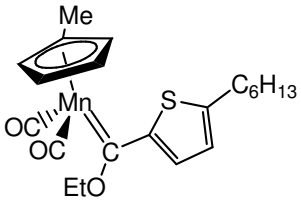

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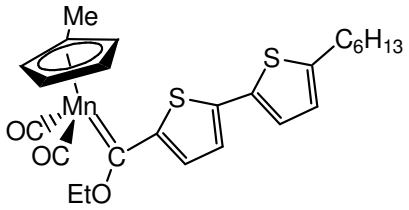

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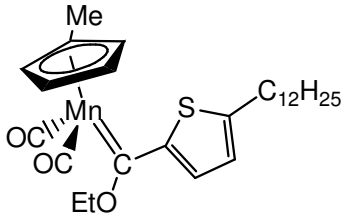

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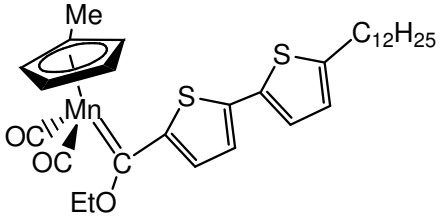

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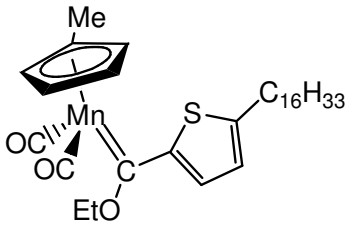

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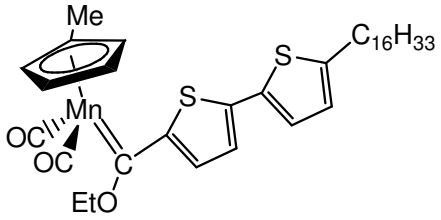

18b

List of Abbreviations

B	Benzene
Bu	butyl
CRT	cathode-ray tube
CAD	computer-aided drawing
Cr	crystal
Cp	cyclopentadienyl
DSC	differential scanning calorimetry
d	doublet
Et	ethyl
FAB	fast atom bombardment
I	isotropic liquid
IR	infrared spectroscopy
vs	very strong
s	strong
m	medium
w	weak
LCD	liquid crystal display
LMM	low molar mass
MS	mass spectrometry
Me	methyl
m	multiplet
N	nematic mesophase
N_D	discotic nematic mesophase
NMR	nuclear magnetic resonance
NLO	non-linear optical
n	director
POM	polarizing optical microscopy
ppm	parts per million

R	alkyl
RF	radio frequency
SmA	smectic A mesophase
SmC	smectic C mesophase
T	thiophene
TT	bithiophene
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TN	twisted nematic display
t	triplet
UV	ultraviolet
XRD	X-ray diffraction

List of Figures

List of Tables