

***THIOLATO SCHIFF BASE COMPLEXES OF NICKEL AND
PALLADIUM AS MESOGENS AND MOLECULAR WIRES.***

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SUPERVISOR: PROFESSOR JAMES DARKWA

ABSTRACT

THIOLATO SCHIFF BASE COMPLEXES OF NICKEL AND PALLADIUM AS MESOGENS AND MOLECULAR WIRES.

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PhD Thesis, Department of Chemistry, University of the Western Cape

Schiff base thiol compounds were prepared by the condensation of 4-aminothiophenol and 4-arylbenzaldehyde or 4-alkyloxybenzaldehyde ($\text{OHCC}_6\text{H}_4\text{OR}$, $\text{R} = \text{C}_6\text{H}_5$, $\text{CH}_2\text{C}_6\text{H}_5$, $\text{C}_n\text{H}_{2n+1}$, $n = 4, 6, 8, 10, 12, 14, 16, 20$) and 1,4-aryldialdehyde. Monoaldehydes formed $\text{HSC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OR}$ (**A**) whilst dialdehydes formed $\text{HSC}_6\text{H}_4\text{NC}(\text{H})\text{ArC}(\text{H})\text{NC}_6\text{H}_4\text{SH}$ ($\text{Ar} = 2,5$ -thiophene, 1,3-benzene, 1,4-benzene and 4,4'-biphenyl) (**B**). Compounds **A** and **B** reacted with $\text{NiX}(\text{PR}_3)(\eta^5\text{-C}_5\text{H}_5)$ ($\text{X} = \text{Cl}$ or Br , $\text{R} = \text{Ph}$ or Bu) to give mononickel complexes, $\text{Ni}(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OR})(\text{PR}_3)(\eta^5\text{-C}_5\text{H}_5)$ (**C**) and dinickel complexes, $(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)\text{Ni}(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{ArC}(\text{H})\text{NC}_6\text{H}_4\text{S})\text{Ni}(\text{PR}_3)(\eta^5\text{-C}_5\text{H}_5)$, (**D**) in high yields.

Compounds **A** reacted with nickelocene and diethyldithiocarbamatonicel(II) bromide to form $[\text{Ni}(\mu_2\text{-SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OR})(\eta^5\text{-C}_5\text{H}_5)]_2$ (**E**) and $[\text{Ni}(\mu_2\text{-SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OR})(\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2)]_2$ (**F**) respectively in low to moderate yields. Complexes **E** were also prepared from the reaction of $[\text{Ni}(\mu_2\text{-SC}_6\text{H}_4\text{NH}_2)(\eta^5\text{-C}_5\text{H}_5)]_2$ and $\text{OHCC}_6\text{H}_4\text{OR}$ ($\text{R} = \text{OC}_n\text{H}_{2n+1}$, $n = 4, 6, 14, 16$) in low to moderate yields. The complexes, bearing terdentate ligands, $(\text{C}_6\text{H}_3(\text{CH}_2\text{NEt}_2)_2)\text{PdSC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ ($n = 6, 12$) (**G**), $(\text{C}_6\text{H}_3(\text{CH}_2\text{S}^i\text{Pr}_2)_2)\text{PdSC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OC}_6\text{H}_{13}$ (**H**) and $(1,2\text{-SC}_6\text{H}_4\text{NC}(\text{H})\text{-}2\text{-C}_5\text{H}_4\text{N})\text{NiSC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$ ($n = 14$ and 16) (**I**), were produced from the reactions of **A** with $\text{C}_6\text{H}_3(\text{CH}_2\text{NEt}_2)_2\text{PdBr}$, $\text{C}_6\text{H}_3(\text{CH}_2\text{S}^i\text{Pr}_2)_2\text{PdBr}$ and $(1,2\text{-SC}_6\text{H}_4\text{NC}(\text{H})\text{-}2\text{-C}_5\text{H}_4\text{N})\text{NiCl}$.

Thermal analysis data of compounds **A**, **C**, **F** and **I** established that they were non-mesogenic while **E** and **G** were found to be mesogenic. The lack of mesogenic behaviour of **A** could be attributed to hydrogen bonding. The non-mesogenic behaviour of **C** and **F** is due to reduced molecular anisotropy as a result of large lateral substituents. Complexes **I** decomposed at high temperatures and before melting and hence no liquid crystalline behaviour was found. It is likely that the high decomposition temperature is the result of increased molecular interactions. We found that removing the phosphine ligands and increasing molecular length induced liquid crystalline behaviour in complexes **E**. The more planar complexes **G** were also found to be liquid crystalline.

Cyclic voltammetry was used to probe the electrochemistry of compounds **D**, **E** and **F**. For the α,ω -dithiolato Schiff base complexes of nickel (**D**), we found that the dithiolato bridge allow electronic interaction between the two nickel centres. This was established from ΔE values between the two redox couples found in such complexes. These ranged from 296 mV to 300 mV, which are higher than the minimum value required for electronic interaction between two metal centres. Therefore the α,ω -dithiolato Schiff base compounds behave as molecular wires. Complexes **E** on the other hand, undergo two simultaneous one-electron redox processes with no electronic interaction between the two nickel centres. Compounds **F** undergo irreversible electrochemical processes, implying that the electron transfer processes are followed by chemical reactions.

Date: May 2003

DECLARATION

I declare that “*Thiolato Schiff base complexes of nickel and palladium as mesogens and molecular wires*” is my own work, that it has not been submitted for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

RICHARD MOTLHALETSI MOUTLOALI.

MAJ 2003
.....

Date

Moutloali R.M.
.....

Signature

ACKNOWLEDGEMENTS

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The Organometallics Research Groups of Professors Darkwa and Mapolie, University of the Western Cape, for everything. Those weekly meetings and “seminars” were a real eye opener and good experience.

Finally the Department of Chemistry, its staff and students, for having been a good host.

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Part of the work contained in this thesis has been published. A list of the publications with the title and authors follows.

1. *Synthesis and thermal behaviour of cyclopentadienylnickel(II) thiolato complexes. Crystal structures of $Ni(\eta^5-C_5H_5)PBu_3(SC_6H_4NC(H)C_6H_4C_6H_5)$ and $Ni(\eta^5-C_5H_5)PBu_3(SC_6H_4NC(H)C_6H_4OC_4H_9)$.*

R.M. Moutloali, J. Bacsá, D.A. Ddamba and J. Darkwa; *J. Organomet. Chem.* 2001, 629, 171

2. *[2,6-Bis(isopropylthiomethyl)phenyl- K^3S,C^3S']bromopalladium(II)*

R.M. Moutloali, J. Bacsá, and J. Darkwa; *Acta Cryst. Sec C.*, 2002, C58, M109

3. *Bimetallic nickel complexes with bridging dithiolato Schiff base ligands: synthesis, mass spectral characterisation and electrochemistry*

R.M. Moutloali, F.A. Nevondo, J. Darkwa, E. Iwuoha, and W. Henderson; *J. Organomet. Chem.* 2002, 656, 262

Dedication

To my family: my mother, my brothers: Selepe, Matsie, Nyadiwa and my beloved sister: Ntsoaki, and my late grandmother, who passed away during my PhD studies. To Maite, my friend and companion, and to Mathabo.

Chapter 1

Introduction to metal thiolate chemistry.

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1.1 General areas of transition metal thiolate research.

The chemistry of metal complexes containing thiolate ligands (L_nM-SR) has developed extensively over the last several decades.¹ They are an enormously rich class of compounds and are presently a subject of great interest in chemistry. As typical soft ligands the electron-rich thiolate groups (RS^-) and their multifunctional homologues $^-SRS^-$ have a great affinity for a large number of metals. The electronic and steric capabilities offered by the monodentate and bidentate chelates have been used to stabilize a broad spectrum of mononuclear, oligomeric and polymeric metal complexes with new and remarkable structures and properties. The thiolate ligands (RS^- and $^-SRS^-$) are capable of extreme variations in their coordination and bonding to metals. The monofunctional ligand, RS^- , can bond in a monodentate² (A), μ_2 -bridging³ (B) or μ_3 -bridging manner⁴ (Chart 1.1). The coordination possibilities offered by the bifunctional thiolate anion, $^-SRS^-$, are even greater.⁵

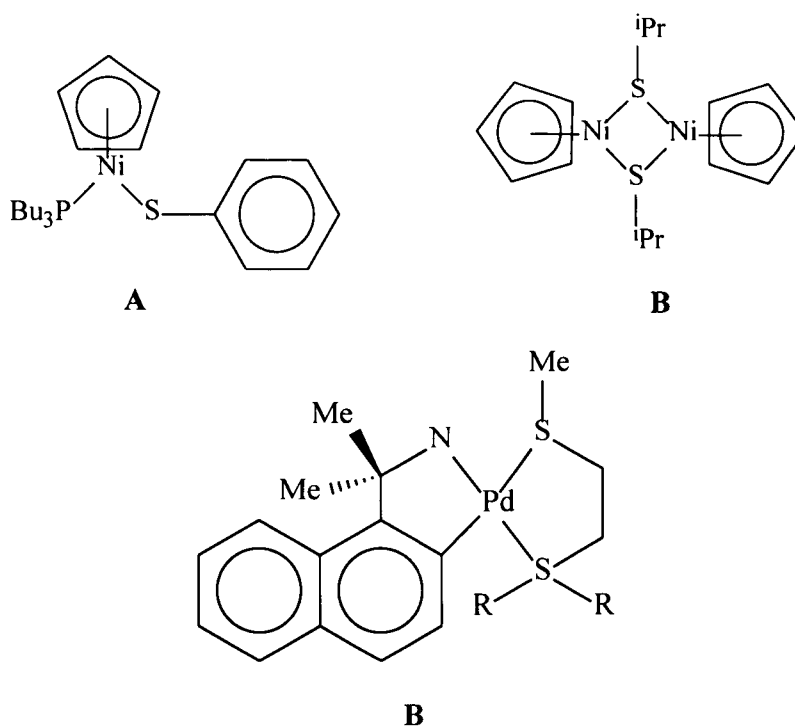


Chart 1.1: Typical binding modes of sulfur.

Metal thiolates are important for several applications; these are highlighted in the next two paragraphs. Metal centres with complete or partial sulfur coordination play an important part in the chemistry of life processes. Examples of this are provided by electron transferases such as the redox metalloprotein of iron, the ferredoxins, and oxidoreductases such as nitrogenases like plastocyanin, azurin and ceruloplasmin.⁶ Thus metal thiolates are extremely useful as models for metalloproteins⁷ and metalloenzymes⁸. Gold thiolates are also of importance as drugs, especially for the treatment of arthritis.⁹

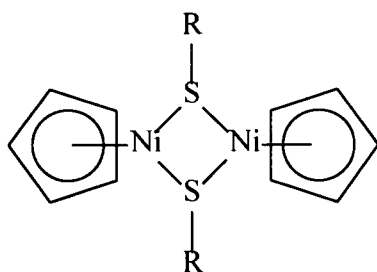
A new and interesting development is the use of volatile molecular metal thiolates as starting materials for chemical vapour deposition (CVD) of metallic or sulfidic surface layers.¹⁰ Metal thiolates also feature as models for hydrodesulfurisation (HDS) and in other catalytic systems.¹¹ In addition to the above, metal thiolates have potential applications in such diverse fields of material science from electronic (molecular) conductors¹² to liquid crystals¹³ and nonlinear optical (NLO)¹⁴ materials and as SO₂ absorbers or scrubbers¹⁵. Since the chemistry of metal-sulfur complexes is so wide, this

section will only deal with the following areas of interest: (i) metal thiolates as models for hydrodesulfurisation catalysis, (ii) metal thiolates as SO₂ absorbers and as catalysts, (iii) molecular or electronic conductors and (iv) as liquid crystals and nonlinear optical materials; since the metal thiolate reported in this thesis resemble complexes that have the above properties.

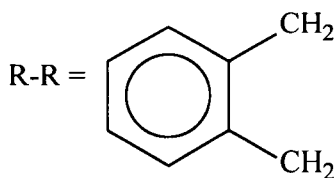
1.2 Metal thiolates as models for hydrodesulfurisation (HDS) catalysis.

Metal thiolates have been extensively studied as HDS catalysts.¹⁶ The mechanism of the HDS process¹⁷ is of interest to many inorganic chemists, because the catalytic action is poorly understood. Thus it provides an opportunity to prepare model compounds that can be used to mimic the heterogeneous process in homogenous reactions, metals such as Co, Ni and Nb are predominantly used in such studies.¹¹

Mechanistic investigation of the carbon-sulfur bond reduction with organometallic reagents under homogeneous conditions may provide useful information on the actual mode of heterogeneous desulfurisation reactions. Reactions of metal thiolates give molecular-level insights into these HDS processes by providing the structures and behaviour of molecular analogues.¹⁸ The ligation between the sulfur moiety and certain metals, such as Ni, Ti, Ru and Rh, activate the carbon-sulfur bond. The C-S bond cleavage is initiated thermally, photolytically or upon hydrogenation.¹⁹ Ho *et al.* studied the reductive cleavage of the C-S bond using LiAlH₄ in a series of complexes with a μ_2 -sulfur bridge that have the general structure I.



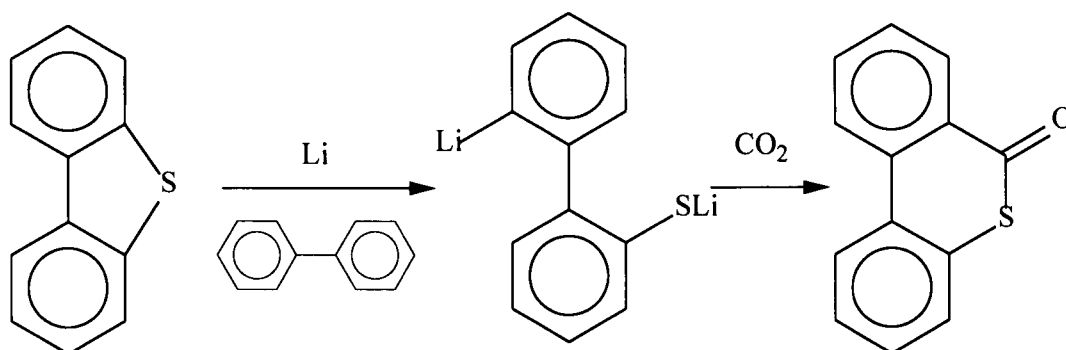
R = Ph, PhCH₂, 2-naphthyl, n-C₈H₁₇, R-R.



I

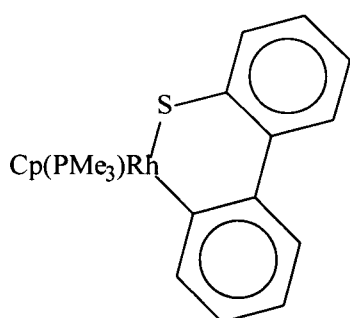
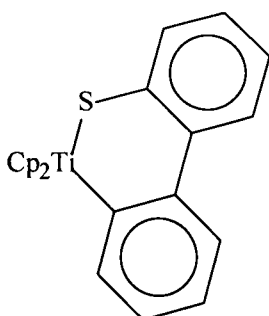
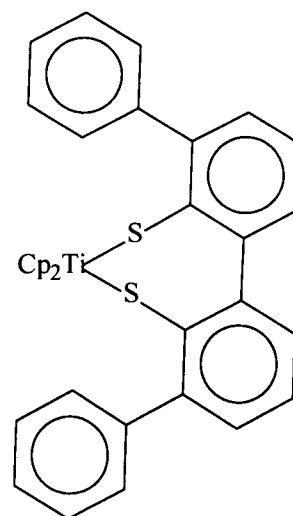
The Ho model suggests that the carbon–sulfur bond is activated by complexation with nickel and subsequent hydride transfer afford the corresponding reduced hydrocarbon. This result points to the role the hydridic species plays in the reduction. Yamamoto *et al.* on the other hand report that C-S bond reduction occurs upon thermolysis of the hydridothiolatonickel phosphine complexes²⁰ that indeed supports the involvement of the metal hydride in the C-S bond cleavage. The products from the reduction of the μ_2 -sulfur complexes with LiAlH₄ were benzene, toluene, decane, naphthalene and o-xylene, which all lack sulfur atoms.

Another good example of C-S bond activation is the reduction of dibenzothiophene (DBT) first reported in 1957 by Gilman and Dietrich.²¹ This reduction was later improved on by Eisch.²² DBT is one of the major sulfur-containing contaminants in fossil fuels and is amongst the most difficult compounds to desulfurise.²³



Scheme 1.1

Industrially these sulfur heterocycles are hydrogenolysed in HDS process by the action of metal catalysts to give hydrocarbons and hydrogen sulfide.²⁴ Thus the syntheses of metal complexes from sulfur-containing heterocycles is viewed as a way to study the mechanistic reactions of the HDS process by scientists.²⁵ Access to dibenzothiophene (BDT) metal complexes is generally *via* preactivation of the BDT (Scheme 1.1), followed by reaction with various organometallic fragments.² Some of the examples of HDS catalysts are **II**, **III** and **IV** shown below.²

**II****III****IV**

In using the compounds **II**, **III** and **IV** above as HDS catalysts, it was found that the sulfur to metal ratio was crucial. Only low sulfur-to-metal ratios led to desulfurisation,

whereas high sulfur to metal ratios actually formed organosulfur compounds such as thiophene.² Nevertheless the above study is a demonstration of how metal-thiolates can be used as models for HDS catalysis.

1.3 Metal thiolates as sulfur dioxide absorbers.

The ability of metal thiolates to absorb sulfur dioxide is another potential application for these complexes. Researchers are interested in the ability of metal thiolates to absorb sulfur dioxide, both reversibly and irreversibly, and its kinetics.² The research is driven by the need to remove the hazardous SO₂ from the environment. The combustion of fossil fuels and the roasting of metal sulfide ores is the primary cause of atmospheric sulfur dioxide pollution. One possible solution to this problem is to trap SO₂ before it is released into the atmosphere and research directed at solving the problem has led to reactions of metal thiolates with sulfur dioxide. In these complexes the sulfur dioxide can either bind to the metal¹⁶ or to the sulfur atom of the thiolate ligand. The former interaction seldom leads to reversible absorption of SO₂, whereas the latter invariably gives products that easily release sulfur dioxide gas; presumably because the ligand-sulfur dioxide interaction is generally weak.

Nickel thiolato complexes are some of the complexes that reversibly bind SO₂ molecules.³ In these complexes the Ni-SR functionality provides an excellent example of the nucleophilicity of the metal thiolates.³ This behaviour of the Ni-SR functionality is exemplified by the reversibility of the binding of SO₂ by (bme-daco)Ni(II) (bme-daco = 1,5-bis(mercaptoethylpropyl)-1,5-diazacyclooctane). Even though the possibility of SO₂ binding to the metal centre exists, it has been shown by X-ray crystallography that SO₂ exclusively binds to the sulfur atom of the thiolato ligand.^e The ability of these complexes to effectively reversibly absorb SO₂ gas effectively and reversibly, is influenced by the substituents on the thiolato ligand. Aryl substituents are found to enhance the reversibility whereas alkyl substituents do not. For example, reversibility of SO₂ absorption was observed for complexes (dppe)Ni(TDT) and (dppe)Ni(1,2-BDT)

(dppe = diphenylphosphinoethane; TDT = toluenedithiol, BDT = 1,2-benzenedithiol) but it was found that SO₂ does not bind to the metal when alkyl analogues are used.³

An alternative solution to the removing of SO₂ as a pollutant can be the activation of S=O bonds in SO₂ by transition metal thiolates, especially when reduced by hydrides and hydrogen.³ For example it has been shown that the complexes [(Me_nCp)Mo(μ-S)(μ-SH)]₂ (Cp = C₅H_{5-n}; n = 0, 1 or 5) and their chromium analogue (Cp^{*}Cr₂S₅; Cp^{*} = C₅Me₅) effectively catalyse the homogeneous hydrogenation of SO₂ to S₈ and H₂O.³

1.4 Metal thiolates as conductors.

The rapid developments in the field of telecommunication and computing devices are pressing the need for improved electronic components. The technology needed will mainly depend on the interplay between electrons and photons. Molecular chemistry offers a unique opportunity to design materials combining several properties (e.g. magnetism, conductivity and nonlinear optics or a combination of the three) that could be coupled in an actual interplay.³

Self assembled monolayer (SAM) structures composed of n-alkanethiol derivatives chemisorbed onto gold surfaces and bearing varying amounts of pendant electroactive species or groups have been shown to be excellent systems in which factors that govern the rate of electron transfer across interfacial barriers could be investigated for conduction.³ Various systems have been studied in order to obtain structure-property relationships that can be used to get a clearer picture of how structural effects could mediate the electron transfer processes.³ In most of the SAMs used, conjugated oligomers are α, ω-dithiol. The thiol functionality is necessitated by the need for binding between proximate gold probes in electronic conduction experiments.³

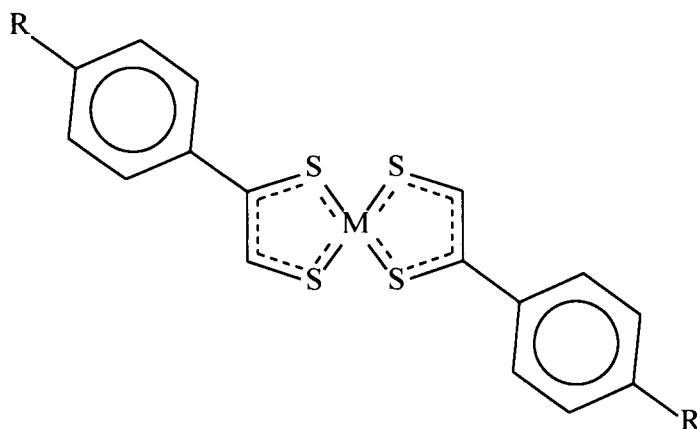
Several ways of introducing the terminal thiol functionality have been described and include; (i) the *in-situ* NH₄OH-promoted deprotection of acetyl protected thiol, (ii) the non-base promoted adsorption of thioacetyl terminated oligomers on gold, to finally form

surface-bound thiolates. When such systems are surface bound via an aromatic thiol unit there is no possibility of any insulation occurring, as there are no alkyl chains to do that.³

Such metal thiolate compounds effectively conduct, through electron movement along the thiolato ligands. When long alkyl or alkoxy chains are attached to thiolato ligands, the metal thiolates tend to behave as liquid crystalline materials and with shorter chains as nonlinear optical materials. Since this thesis deals mainly with metal thiolato complexes that may have potential mesogenic behaviour, a review of metal thiolato complexes with liquid crystalline properties will be given in subsequent sections of this chapter and a more detailed account of metallomesogens, as well as background information about the liquid crystalline state, in chapter 2.

1.5 Metal thiolates with liquid crystalline properties.

Ligands that have sulfur as the donor atom also form metal complexes with liquid crystalline properties. However, prior to the work that is reported in this thesis, all such complexes featured only bidentate thiolato ligands. Giroud and Muller-Westerhoff were the first to systematically study the d^8 (Ni(II), Pd(II) and Pt(II)) metal atoms with dithiolene ligands. The main types of complexes are exemplified by **V**, **VI** and **VII**. X-ray diffraction studies showed that the nickel complex had the expected M(II) square planar geometry, with substituents trans to each other,³ thus providing the platform for the desired packing in the liquid crystalline state.



M = Ni (V), Pd (VI) or Pt (VII), R = C_nH_{2n+1}, n = 4 - 12, .

Figure 1.1: A typical dithiolato liquid crystalline complexes.

The nickel and the platinum complexes form nematic and smectic mesophases. Complexes with $n = 4$ and 5 in Figure 1.1 are nematic and those with $n > 6$ are smectic.⁴ The palladium complexes, however, have no mesogenic properties.⁴ It is surprising that the palladium analogues have no mesogenic behaviour, since the structural and electronic properties of these palladium complexes are similar to those of the nickel and platinum complexes.

Other types of thiolato complexes found to be mesogenic are the bis(4-alkoxydithiobenzoato) complexes of nickel(II) and palladium(II) (Fig. 1.2).⁴ These complexes are structurally similar to those synthesised by Giroud and Muller-Westerhoff in 1978 but have alkoxy chains instead of alkyl chains and a 4-membered metallo-ring instead of a 5-membered ring.⁴ Optical microscopy, combined with X-ray diffraction and differential scanning calorimetry (XD-DSC) study, confirmed the formation of smectic C, S_c, mesophases for the palladium complexes with longer chains ($n \geq 8$) and of N phases for shorter chains ($n = 4, 5$).⁴ The nickel analogues showed similar results. Using the same ligand system as for groups V and VI metal complexes (Cu, Zn and Hg) with complex coordination geometries can be prepared. For example the zinc compound was found to be monomeric in solution, but binuclear in the solid state forming an eight

membered $Zn_2S_4C_2$ ring.⁴ The related mercury complexes $(Hg(S_2CC_6H_4OC_nH_{2n+1})_2$ ($n = 4, 8$) were found to possess intermolecular $Hg...S$ interactions in the solid state. They have two shorter trans $Hg-S$ bonds (2.41 Å) and two longer trans $Hg-S$ bonds (2.96 Å) in the same plane, but also had two additional axial intermolecular $Hg...S$ contacts (3.36 Å).^{3 b} Both the four membered metallo-sulfur ring and the five membered metallo-sulfur ring give rise to calamitic mesogens. However complexes with aromatic rings exhibit smectic mesophases as opposed to nematic phases produced by complexes with non-aromatic rings.

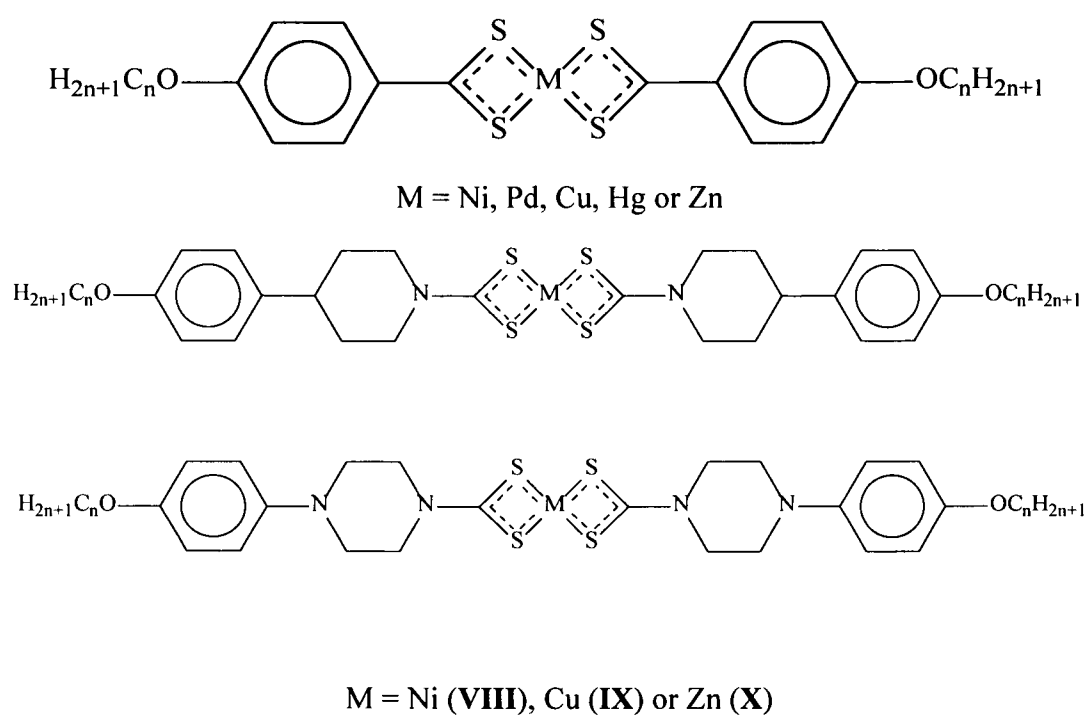
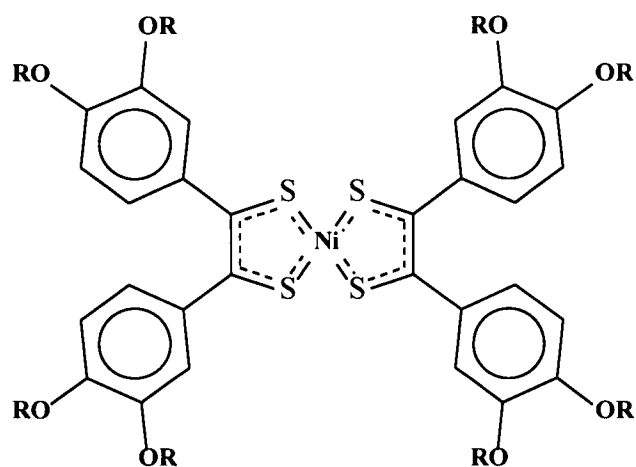


Figure 1.2: Dithiolato mesogens with a four-membered metallo-sulfur ring.

In addition to these calamitic mesogens, metal-sulfur complexes that form discotic mesogens are known.⁴ For example a nickel complex with four 3,4-bis(dodecyloxy)phenyl substituents, **XI**, characterised by X-ray diffraction, was found to form hexagonal disordered columnar mesophases (D_{hd}).⁴



XI

In spite of a fairly good number of bidentate dithiolato metallomesogens in the literature, there are no known examples of simple monothiolato metal complexes with mesogenic behaviour.

The research work reported in this thesis was undertaken to initially investigate the use of monothiols to prepare nickel thiolate mesogens. It later developed into the use of both mono- and dithiols in forming nickel and palladium thiolates. The section below thus outlines the final objectives of the research projects reported in the thesis.

1.6 Rationale and Objectives.

The literature that is devoted to dithiolates as ligands for metallomesogens chemistry is voluminous. On the other hand there is virtually no literature report on monothiols as ligands for metallomesogens. Therefore this thesis is an investigation on the use of monothiols as ligands for the preparation of metallomesogens. Secondly it deals with the study of the effects bulky ancillary ligands have on the thermal properties of compounds that are studied as liquid crystals. Most compounds that are studied for their liquid crystal behaviour have small lateral substituents and thus seek to retain the molecular shapes of their promesogenic ligands. Thirdly, this study compares the different shapes of molecules with respect to their mesogenic behaviour based on the size of the lateral substituents, the molecular lengths and the geometry around the metal atom.

Chapter 4 deals with the study of dithiol Schiff base compounds as bridging ligands for nickel compounds. This was done with the aim of probing the molecular wire ability of the dithiol Schiff base bridges. Most compounds that are studied for their molecular wire ability have purely carbon functional groups such as alkene and alkynes as linkers between aromatic rings. In such compounds the ligand is bound to the metal via a metal-carbon σ -bond. In the present study we have used the imine group as a linker and a metal-sulfur bond instead of the conventional metal-carbon bond. This was done with the view that most studies on electronic conduction in organic molecule-solid (usually gold) electrode nanojunctions, the binding sites are usually a sulfur atom. Rarely is a metal-sulfur bond used in solution state studies of molecular wires studies. Cyclic voltammetry was the technique of choice due to its simplicity and the fact that it does not depend on thermodynamic factors but only on the static spectroscopic parameters.