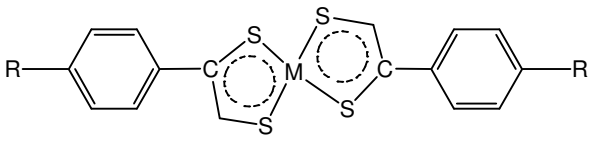
Chapter 2

Nickel(II) complexes with thiophene-containing ligands

2.1 Introduction

Many classical inorganic nickel(II) complexes with rod-like structures and N and/or O donor-atom ligands, such as bidentate β-enaminoketones[1,2], tropolonates[3] and salicylaldimine[4] have been studied for their liquid crystalline properties. Disc-shaped nickel(II) mesogens have been reported with phthalocyanine[5,6] and alkoxy hydrazine[7] ligands.

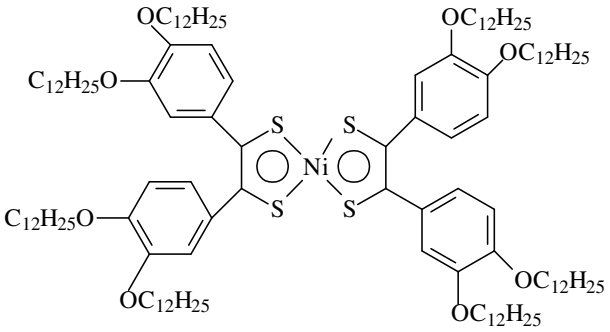
An important class of nickel(II) complexes are those with sulfur donor-atoms such as thiols, dithiolene and dithiocarboxylate as ligands[8,9]. The chemistry of nickel(II) thiolate complexes has attracted attention and has been studied widely because of the identification of nickel in the active site of the enzyme hydrogenase in biological systems[10]. Since the colour remains an important issue in liquid crystalline displays the role of nickel(II) in liquid crystalline materials must not be underestimated for potential application[11,12]. The first mesogenic nickel(II) complexes were those with dithiolene ligands and were studied by Giroud and Muller-Westerhoff, in 1977[13].



M = Ni, Pd, Pt

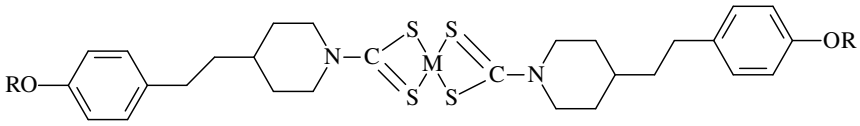
The first example of a nematogenic nickel(II) metallomesogen reported was a complex substituted with terminal butyl chains[13] (above). For compounds with longer alkyl chains, smectic mesomorphism was observed. The nickel(II) and platinum(II) complexes displayed enantiotropic mesophases, which were nematic for the shorter chains and smectic for the longer alkyl chains while the corresponding palladium complexes did not show any mesomorphic properties. As intermolecular forces play an important role in the mesophase character, the lack of mesomorphism may be due to the strong Pd-Pd bond.

In addition to the calamitic (rod-like) metallomesogens, Ohta *et al.*[14] reported disc-shaped metallomesogens for nickel and dithiolenes. Nickel(II) dithiolene with four 3,4-bis(dodecyloxy)phenyl substituents was shown by X-ray diffraction to give rise to a hexagonal disordered columnar (discotic) mesophase.



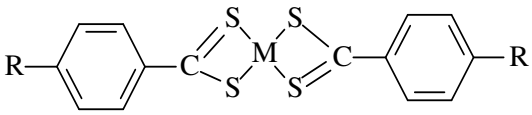
Of the piperazine dithiocarbamate complexes of palladium, nickel, copper and zinc only the nickel and copper derivatives showed liquid-crystalline behaviour[15]. Both the nickel and copper complexes showed similar phase behaviour for the

hexyloxy chain. On cooling from the isotropic liquid a highly birefringent, schlieren texture of smectic C was observed.



M = Pd, Ni, Cu, Zn

The mesogenic properties of bis(p-alkylphenyldithiolate) complexes of nickel(II) and platinum(II) were reported by Mueller-Westerhoff in 1980[16].



M = Ni, Pt; R = alkyl or alkyloxy substituents

In 1988 Adams *et al.*[17] synthesized the mesomorphic 4-alkyloxydithiobenzoate derivatives of Ni, Pd and Zn. The mesomorphism of nickel(II) and palladium(II) complexes were similar, showing smectic C phases for longer alkyl chains ($n \geq 8$). In general, the melting points of the palladium complexes were 20-30^{o}C higher than those of the nickel complexes, whereas clearing points were about 80^{o}C higher.

Adams *et al.*[18] as well as Ohta and co-workers[19] undertook detailed studies on the liquid crystalline properties of 4-alkyloxydithiobenzoate derivatives. The 4-alkyloxydithiobenzoates of Zn, Ni and Pd are highly dichroic and can be used in liquid crystal displays. The strongly coloured mesomorphic dithiolates prepared by Giroud and Muller-Westerhoff[16] were investigated as potential dyes in guest-host systems, by incorporation of the mesomorphic derivatives into nematic hosts[20]. The linear dichroism of the 4-alkyloxydithiobenzoates of nickel(II) was

also measured by the Sheffield group[21] in the nematic solvent and reported that those complexes were not suitable as dyes for displays.

In 1988 Ohta *et al*. employed alkyldithiocarboxylate as ligands to form dimeric nickel(II) complexes that exhibited monotropic smectic phases[22]. They also employed alkoxydithiocarboxylate to form monomeric nickel(II) complexes that exhibited double and triple melting behaviour. In nickel(II) and platinum(II) complexes the dispersion forces are more dominant and dissociation into the monomer is possible at the temperature of the mesophase.

Earlier literature (1963-1975) have revealed nickel(II) complexes (d^8 electron configuration) displaying a variety of coordination numbers and many different coordination modes for thiol, dithiocarboxylate, dithiocarbamate and trithiocarboxylate ligands[8]. Square-planar, tetrahedral, 5-coordinate, and octahedral geometries are known for nickel(II) with dithiocarboxylate ligands. It has been widely demonstrated that square-planar or square-pyramidal coordination leads to the appearance of liquid crystalline properties, whereas tetrahedral geometry usually inhibits mesophase formation. All the mesomorphic complexes are diamagnetic, which has been interpreted to indicate a square-planar coordination about the metal.

In this study the reactions of a series of 5-alkyl-2-thiophenedithiocarboxylates with nickel(II) chloride were investigated to see if the inclusion of thiophene in the chain would affect the outcome of the reactions and play a role in determining

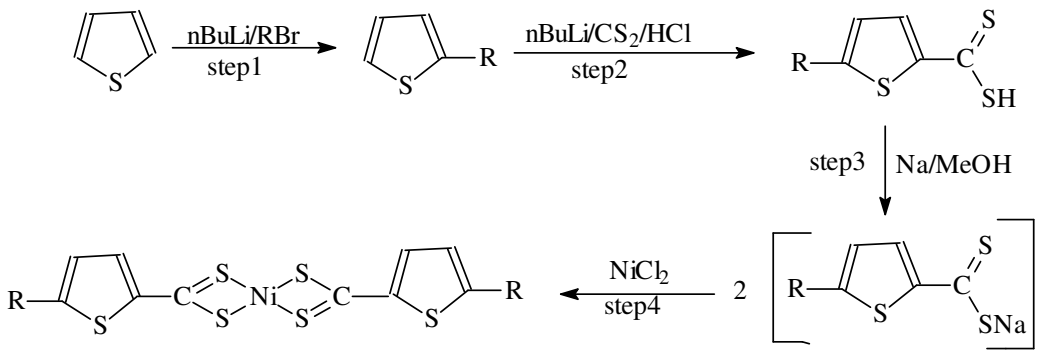
the melting point behaviour and properties of mesophases. Reactions of dithiocarboxylates and derivatives were extensively studied and resulted in some fascinating chemistry and new structurally interesting complexes[8].

2.2 Results and discussion

2.2.1 Synthesis and characterization

Five complexes of the type $[Ni(S_2CTR)_2]$ (where T = 2,5-disubstituted thiophene, R = alkyl group; C_4H_9 (**1**), C_6H_{13} (**2**), C_8H_{17} (**3**), $C_{12}H_{25}$ (**4**), $C_{16}H_{33}$ (**5**)) were synthesized via a four-step reaction sequence as shown in Scheme 2.1.

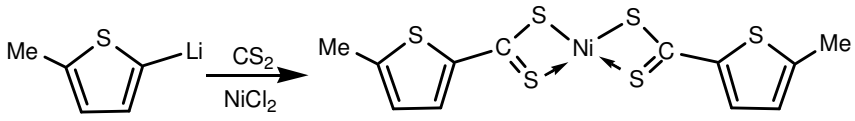
The reactions with butyl lithium were carried out with nitrogen-saturated, dried solvents and in an inert atmosphere. The procedure that was used is similar to the one described by Brandsma[23] for the lithiation of thiophene. Step 1 involved the lithiation of thiophene on position 2 followed by the subsequent addition of alkyl bromide. In the second step 2-alkylthiophene was converted into 5-alkyl-2-thiophenedithiocarboxylic acid. It involved the lithiation of alkyl thiophene on position 5 followed by the addition of CS_2, resulting in a deep red colour. On further acidification with dilute hydrochloric acid, 5-alkyl-2-thiophenedithiocarboxylic acid was formed. Subsequently this acid was converted into the sodium salt by reacting with sodium methoxide, again in an inert atmosphere, in the third step. All the intermediates were isolated.



R = alkyl group; C_4H_9 (**1**), C_6H_{13} (**2**), C_8H_{17} (**3**), $C_{12}H_{25}$ (**4**), $C_{16}H_{33}$ (**5**)

Scheme 2.1

The final step was similar to that of Adams *et al.*[18] who prepared complexes with dithiobenzoate ligands. The addition of a pale green solution of nickel(II) chloride to a stirred solution of sodium 5-alkyl-2-thiophenedithiocarboxylate in water, lead to a change in the colour of the reaction mixture from dark red to blue-violet. The mixture was allowed to stir for 3 hours at room temperature to ensure completion of reaction. The product was precipitated by adding excess methanol and separated by filtration and dried. The colours of complexes **1** and **2** were blue whereas the colours of **3**-**5** were violet. Further purification was done on a silica gel column and the product was purified with hexane/CH_2Cl_2 (4:1) as the eluent. IR and NMR spectroscopy were used to characterize the complexes (**1-5**).



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Scheme 2.2

In a second method (one-pot reaction), 2-methylthiophene was lithiated by butyl lithium at –20°C in THF. The colour of the solution immediately changed to orange on addition of the BuLi, but changed gradually to yellow after stirring for 30 minutes. The mixture was cooled to -50°C and carbon disulfide was added. The mixture became dark red in colour and was stirred for 30 minutes. Anhydrous nickel(II) chloride was added in small portions and the mixture was allowed to reach room temperature. The yellow solid material gradually dissolved on reacting and the solution changed first to green then to blue and thereafter to violet over a period of three hours. The blue-violet product was purified by filtration of the reaction mixture through a plug of silica gel, once the solvent was changed to dichloromethane and afforded **6** in very high yield (the yield was more than 80%). From this mixture it was possible to isolate both a blue and violet compound by column chromatography with mixtures of hexane and dichloromethane. The blue compound indicated by **6a** was less soluble in organic solvents compared with the violet compound indicated by **6b**. Spectroscopic data revealed that two different products or isomers were present in the reaction mixture.

In a third experiment, the blue complex **1a** was dissolved in THF and stirred at room temperature. A sample was taken after 1 hour and the ^{1}H NMR spectrum was recorded in deuterated chloroform. As stirring continued the colour of the reaction mixture gradually changed from blue to violet. After 12 hours the conversion was complete and only the violet complex (**1b**) could be isolated from the reaction mixture. A similar result was achieved after stirring **2a** for 10 hours. The blue compound converted into the violet compound and after further analysis of the products it was clear that the blue and violet complexes of **1** or **2** could be

isomers (the blue isomers were indicated as **1a** or **2a** and the violet ones as **1b** or **2b**).

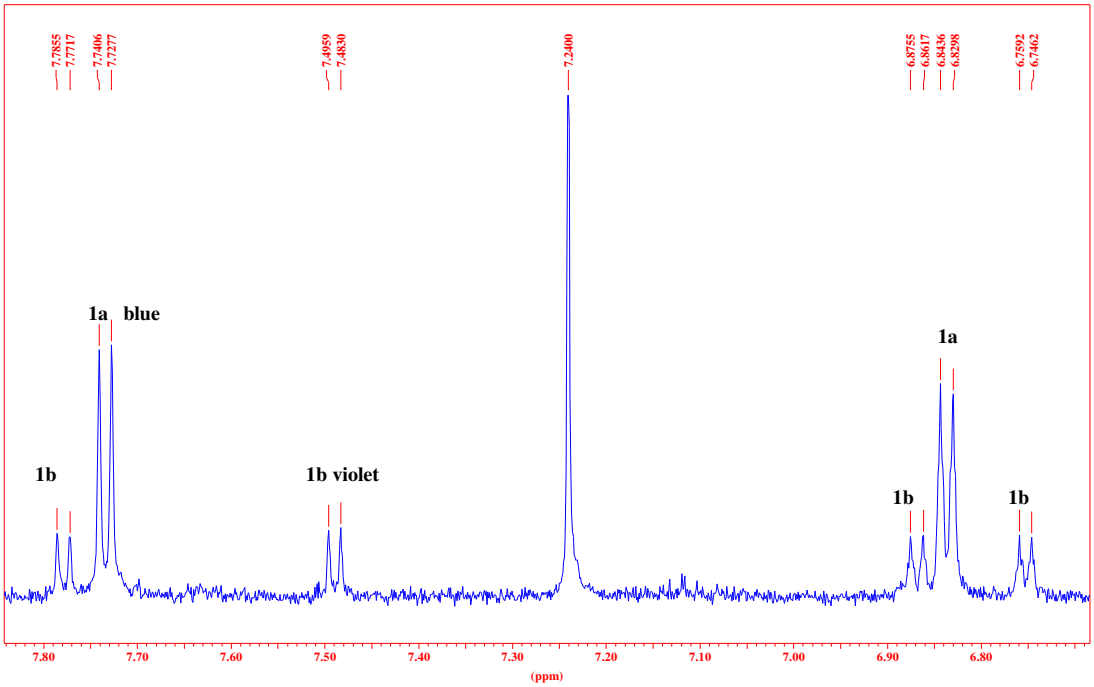


Figure 2.1 ^{1}H NMR spectrum in the thiophene region of **1** (**1a** and **1b**)

In the first method the conversion of the blue isomer into the violet isomer is very slow. In the second method the conversion is much faster, indicating that the solvent facilitates the conversion. THF is a reasonably strong coordinating solvent to transition metals and will assist in stabilizing intermediates during ligand displacement. Figure 2.1 represents the ^{1}H NMR spectrum of compound **1** (**1a** and **1b**) in the thiophene region after withdrawing a sample from the reaction mixture. The sample was taken after 1 hour stirring at room temperature in THF according to the third experiment above. The spectrum shows a mixture of two compounds in different concentrations as indicated by the two sets of resonances. It is

important to note the sharp signals of high resolution for the different protons in the ^{1}H NMR spectrum. This is indicative of diamagnetic and not paramagnetic complexes and implies that the nickel complexes could be square planar or maybe octahedral, but not tetrahedral.

In the first set of resonances, two strong doublets at 7.73 and 6.83 ppm appear in the thiophene region indicating two protons in different electronic environments. This is as a result of the two different substituents in the 2- and 5-positions of the thiophene ring. If **1** has two or more thiophene-containing ligands it means that they are all coordinated to the nickel in a similar fashion. The structures proposed in Figures 2.2 and 2.4 are possible structures that meet this requirement. Similar two-signal resonances were observed for all the blue isomers in the thiophene region of this study.

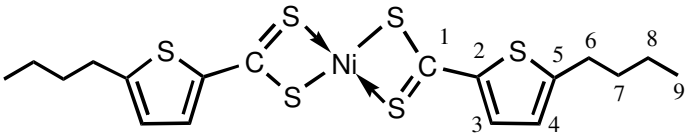


Figure 2.2 Proposed structure of the blue compound, **1a**, with atom numbering

Examples of complexes with two bidentate dithiocarboxylate or dithiocarbamates ligands surrounding one nickel(II) metal have been documented before and a crystal structure determination of $[Ni\{S_2CPh\}_2]$ revealed a flat, square-planar mononuclear nickel(II) complex[24].

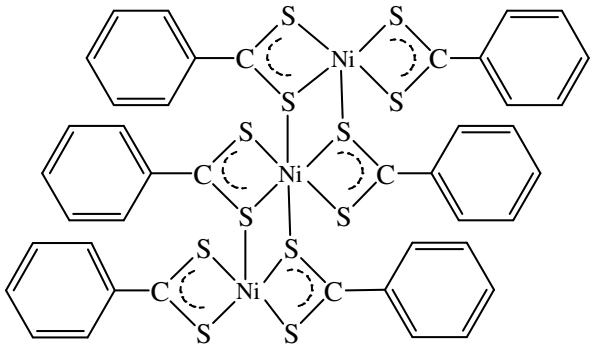


Figure 2.3 Intermolecular interactions between the nickel and sulfur atoms in the solid state of the mononuclear nickel(II) complexes[24]

Structural work confirmed some intermolecular sulfur-metal interaction between chains of square planar complexes for mononuclear [Ni(dithiobenzoate)$_2$] and [Pd(dithiobenzoate)$_2$] complexes in the solid state (Figure 2.3). This interaction will affect the coordination numbers and geometry of the nickel centres in the clusters of three mononuclear complexes. The carbon and the hydrogen attached to the carbons are numbered as shown in Figure 2.2. The carbon in the CS_2 unit is indicated as C1, this procedure of numbering atoms is in line with thiophene numbering schemes where S takes the 1-position. The nickel(II) complexes give deep blue solutions[24,25]. Similar complexes have been reported for diethyldithiocarbamates[26], xanthates[27] and dithiophosphates[28].

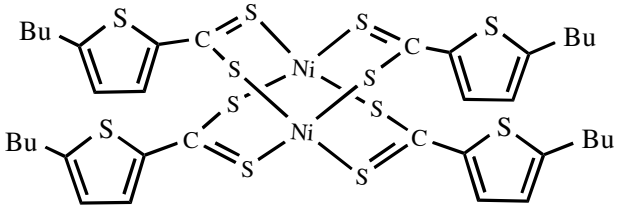
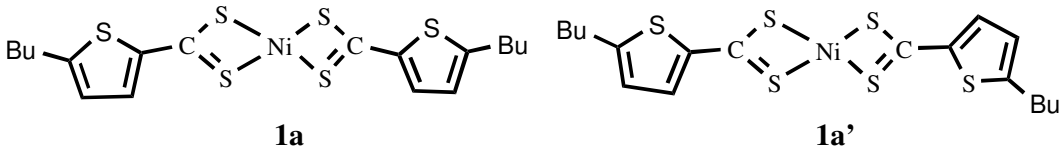


Figure 2.4 Structure of dimeric nickel(II) complexes with bridging R-CS_2 ligands

Another structural type to be considered for **1a** is a dinickel(II) structure with only bridging R-CS_2 ligands (Figure 2.4)[29]. Such a complex will also afford only two doublets of different chemical shifts in the ^{1}H NMR spectrum. Complexes of this kind are quite common and structural data were obtained from single crystal X-ray determinations of $[Ni_2\{S_2CCH_3\}_4]$[30] and $[Ni_2\{S_2CCH_2Ph\}_4]$[31,32]. These complexes were reported to have a red-brown colour in the solid state and in solution[30,32]. Based on the above information, the colours of the reported complexes and the spectral data, the blue isomers **1a**, **2a** and **6a** were assigned to be monomeric, square planar nickel(II) complexes with two terminal bidentate dithiocarboxylate ligands (see Figures 2.2 and 2.10).

Also visible in the thiophene region of the spectrum of **1** (**1a** and **1b**) in Figure 2.1 are four doublets of much weaker intensities. These resonances belong to the spectrum of a second compound, described as the violet compound. The four doublets indicate that there are two thiophene ligands in different electronic environments. Two possible monomeric forms of the complex with composition $[Ni\{S_2C\text{-thiophene-Bu}\}_2]$ can be considered, i.e. **1a** and **1a'** (Figure 2.5). It is known in carbene chemistry that complexes with thienyl substituents may display restricted rotation around the thienyl-carbene carbon bond, resulting in the formation of two isomers with different positions for the sulfur atoms in the thiophene rings[33]. This was ascribed to charge transfer from the thiophene ring via the π-system to the electrophilic carbene carbon atom. A similar situation may exist for an electrophilic carbon atom of a CS_2-unit coordinated to a transition metal and attached to the thiophene ring in **1**. In a square planar complex this will

result in the two sulfur atoms being on the same or on opposite sides of the molecule (Figure 2.5), representing a mixture of geometric isomers.



1a **1a'**

Figure 2.5 Mixture of geometrical isomers resulting from restricted rotation

This is not a satisfactorily explanation for the composition of **1b** for a number of reasons. The large differences in chemical shift values would rather indicate either different modes of co-ordination to the nickel(II) by the 2,5-Bu-thiophene-CS_2 ligand or two ligands of totally different composition. The intensities of the resonances of the four protons in the ^{1}H NMR spectrum of **1b** are exactly the same and that would indicate no preference for any one of the two isomers, which is unlikely. Spectra of pure samples of the blue compound, **1a/2a**, are without the violet component, **1b/2b**, and pure samples of the violet compound are without the blue component. Other arguments of importance against the existence of two isomers are different chemical shift values for the two sets of resonances, the large colour difference of the two isomers and an irreversible conversion reaction of the blue into the violet compound.

Many other possibilities exist for mono- and dimeric nickel(II) complexes with RCS_2 ligands and some of the most likely will now be considered and examined. If one of the coordinated sulfur atoms in the chelate ring would change from a thiol and thione to a thiol and thiophene-sulfur, two different types of sulfur donor ligands could be present in the complex (Figure 2.6).

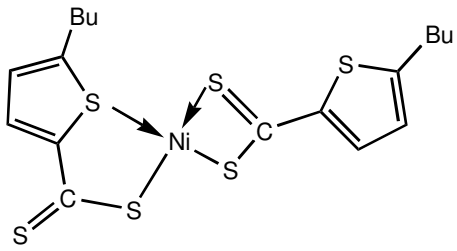


Figure 2.6 Complex with thioether-thiol and thioketone-thiol ligands

These different coordination modes will most definitely result in larger changes in the chemical shift values of the thiophene protons and could also explain the role of THF in the conversion of **1a** to **1b**. Five-membered chelate rings are more stable than four-membered chelate rings that could act as a driving force for the conversion. Arguments against such isomerization processes are the known, poor coordinating abilities of sulfur atoms in thiophene rings to transition metals[34]. This has been ascribed to the involvement of one of the sulfur lone pair electrons in the π-delocalization of electron density over the thiophene ring[35]. Also, in instances where coordination through the thiophene sulfur atom was observed, the sulfur would flip out of the plane of the ring, become sp^3-hybridize and in the process destroy the aromatic character of the thiophene ring[34]. This will result in proton chemical shifts of dienes that are found upfield from the aromatic region. This structural type was eliminated as a possible explanation of the spectral data of **1b** on the basis of the poor coordinating properties of a thiophene sulfur atom.

The conversion and spectroscopic results of **1b** can also be explained by the possibility of two mononuclear nickel(II) complexes forming a dimer by sharing dithiocarboxylate ligands, resulting in one bridging thiophene-containing ligand

for each similar terminal ligand. Two important structures can exist, one with a bridging dithiocarboxylate and the other with bridging sulfur ligands. Figures 2.7 and 2.8 present possible structures of the violet compounds **1b** based on these assumptions.

Structural properties of complexes containing bridging dithiobenzoate ligands in dimetal complexes have been observed for tetrahedrally coordinated Zn(II) and with mononuclear dithiocarbamates tetrahedrally coordinated to Zn(II), Cu(II) and Cd(II) metal centers[17,36].

Complexes of nickel(II) with both terminal and bridging CS_2-ligands and square planar coordination will result in two five-membered chelate rings being perpendicularly orientated if a nickel-nickel bond is assumed. The second isomer, the trans isomer, will have a flat square arrangement of eight atoms. This complex cannot exist because of the small bite angle required by the remaining terminal dithiocarboxylate ligands when forming four membered chelate rings with the nickel centres.

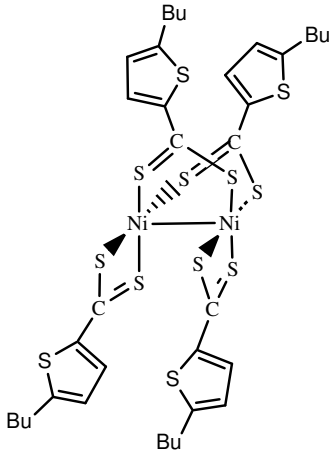


Figure 2.7 Proposed structure of the violet compound **1b**, with bridging CS_2-ligands

As far as we are aware no examples of such *cis*-nickel(II) complexes have been reported but a structure determination of a similar *cis*-[$Pt_2(\mu\text{-dtc})_2(dtc)_2$] (dtc = dithiocumato) complex revealed the coordination modes shown in Figure 2.7[37]. This is a very interesting structural type as on the one side of the complex with the terminal CS_2-ligands, the ligands will form two parallel chains, whereas, they will divert outwards from the metal-metal bond on the other side of the complex. The preferred structures for nickel(II) complexes with bidentate dithiocarboxylate ligands are mononuclear nickel(II) complexes with two terminal dithiocarboxylate ligands when a heteroatom or aryl substituent forms part of the ligands (Figure 2.2)[24] and four bridged dithiocarboxylate ligands when alkyl substituents are part of the ligands (Figure 2.4)[31]. The argument against this type of coordination of RCS_2 for **1b** is that it should generate very similar NMR data compared to **1a**.

Bridging S-ligands, on the other hand, form three membered rings and are again perpendicular in a square planar arrangement of S-ligands around the nickel (II) centers in **1b** (Figure 2.8)[38]. Examples of bridging mercaptide ligands (RS^-) of Ni(II) and terminal trithiocarboxylate ligands are found in literature[38]. The mercaptides form mostly as a result of CS_2 elimination from a trithiocarboxylate ligand and are excellent bridging ligands. As a result of the sp^2-thione carbon in **1b**, now part of the chain and free from being coordinated to the metal, a kink is formed in the chain. This and the orientations caused by substituents in the 2- and 5-positions of the thiophene ring (zig-zag), allows the chains to divert towards the other chains of the terminal CS_2-ligands to still afford a rod-like appearance.

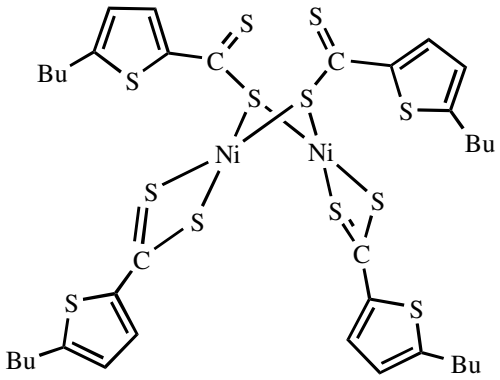
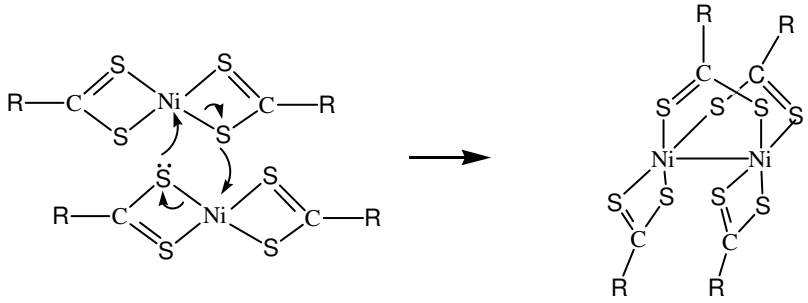


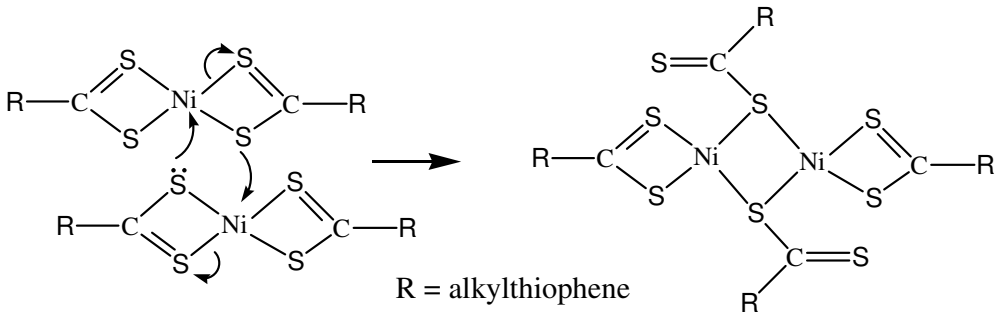
Figure 2.8 Proposed structure of the violet compound **1b**, with bridging S-ligands

Proposed mechanisms for the conversion of a monomer into a dimer for the two classes are presented in Schemes 2.3 and 2.4. The dimer is formed when two monomers interact in an intermolecular fashion. A lone pair of a coordinated sulfur atom of a ligand of the first complex attacks the nickel atom of the second complex and in the process detaches itself from the metal. The same process, but in a reversed way, happens from the second to the first nickel complex. In the process the sulfur atoms of both ligands will bridge two nickel-atoms and form two five- membered rings with two nickel and two sulfur atoms. One ligand remains coordinated to each nickel in the same way as found for the monomer.



Scheme 2.3 Proposed mechanism for the dimerization of nickel(II) complexes with bridging dithiocarboxylate ligands

Even though it is well-known that trithiocarboxylates and dithiocarbamates would readily eliminate carbon disulphide to afford mercaptides or amines (under acidic conditions), we did not in the context of this project, found literature evidence of the elimination of carbon monosulfide from dithiocarboxylates to yield mercaptides. In this case (**1b**) it means that a sulfur atom will rather bridge and not use the available thione sulfur to form a five-membered chelate ring. It is worth mentioning that the coordinating properties of 2-aminocyclopentene-1-dithiocarboxylate were studied and revealed that bonding with metal ions occurred through the amino nitrogen and deprotonated thiol sulfur atoms leaving the thione uncoordinated[39]. Previous arguments of the coordinating abilities of thiophene sulfur atoms ruled out possible competition for a coordination site by this atom (Figure 2.6) as such was the case with amino-dithiocarboxylates. On the other hand, it was assumed that the nucleophilicity of a coordinated sulfur to nickel(II) was too low to compete with an available thione in the coordination to a second nickel(II) center.



Scheme 2.4 Proposed mechanism for the dimerization of nickel(II) complexes with bridging thiol ligands

A more likely explanation can be found by considering a change in the coordination mode of one half of the RCS_2 ligands and thus affording ^1H NMR resonances of the same intensities. A very unexpected, but with well-characterized complex in literature deals with the conversion of one or both of the dithiocarboxylate ligands into a perthiocarboxylate ligand[40,41]. These complexes were originally incorrectly formulated as being disulphide bridged dinickel(IV) complexes with four terminally coordinated dithiocarboxylate ligands and each of the metals in an octahedral ligand environment[42]. It was later shown that these violet or dark red complexes, $[Ni(S_2CR)_2S]$, were in fact mononuclear nickel(II) complexes (Figure 2.9), displaying a four-membered dithiocarboxylato and a five-membered perthiocarboxylato chelate ring[43]. The formation of the sulfur inserted perthiocarboxylato ligand is facilitated by a sulfur source such as S_8 or anionic polysulphides and/or thermal reaction conditions[43-46]. This process can be reversed by abstracting a sulfur atom with PPh_3[45,46]. A further driving force for the S-insertion is the expansion of a four to a thermodynamically favoured five membered chelate ring.

The formation of violet vs blue compounds in this study was contributed not only by the properties of the solvent, but also by the length of the alkyl chain. Using the first method of synthesis the blue monomers are preferred for the shorter chains (C_4 and C_6) and the violet compounds for the longer chains (C_8, C_{12} and C_{16}). By stirring **1a** or **2a** in THF for less than one day the conversion into **1b** and **2b**, respectively, is completed. It should be reasonably easy to eliminate or prove that the mixed mononuclear perthiocarboxylate nickel(II) complexes as being

representative of **1b** – **6b.** This could be done on the basis of chemical analyses, mass spectrometry, literature surveys and spectroscopic methods (NMR and IR).

The atom-numbering scheme adopted in this dissertation for bridging dithiocarboxylate or perthiocarboxylate chelate rings differ from those of terminal dithiocarboxylate ligands only by the addition of an apostrophe to the atom number (Figure 2.9).

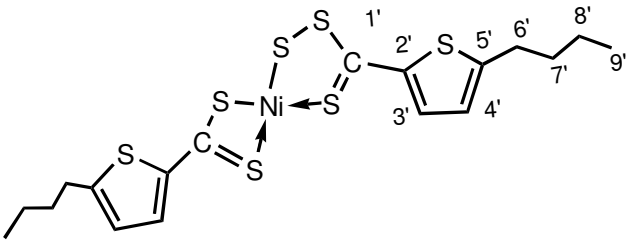
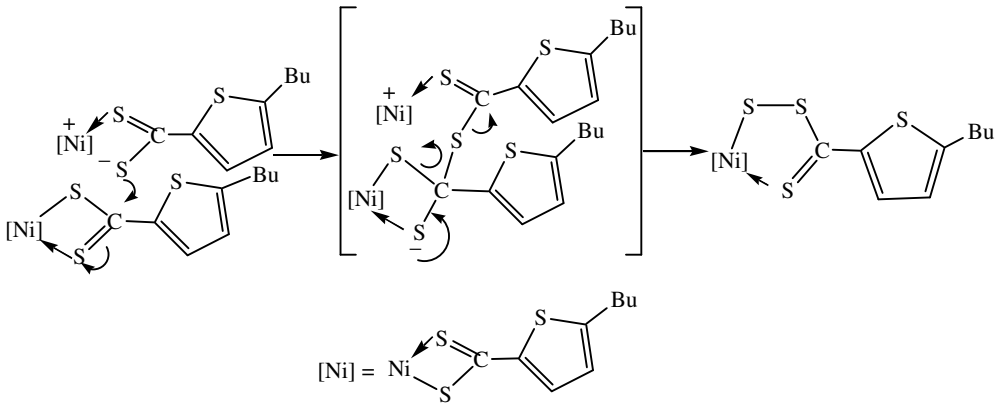


Figure 2.9 Proposed structure of a nickel(II) complex with mixed dithiocarboxylate and perthiocarboxylate ligands

Efforts to obtain single crystals from a wide range of solvents of any of **1b** – **6b**, were unsuccessful. Based on the physical and spectroscopic data and literature results it was concluded that **1b**-**6b** were the mononuclear nickel(II) complexes with perthio and dithiocarboxylate ligands as shown in Figure 2.9. Further confirmation of this structure for **1b** – **6b** was made by literature survey, the violet colour, chemical analyses, and the mass spectral and spectroscopic data. The only outstanding issue was the source of an additional sulfur for insertion. The formation of perthiocarboxylate complexes of nickel(II) have previously been

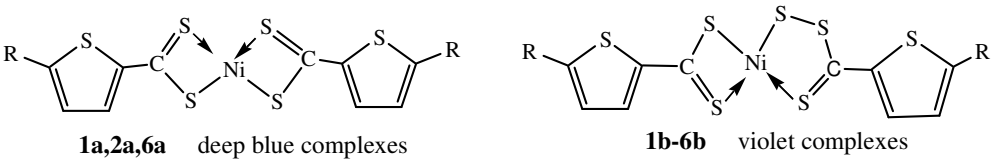
achieved by thermal conditions and the addition of polysulfides, elemental sulfur or by a photolytic procedure in dichloromethane or chloroform[45,46].



Scheme 2.5 Proposed mechanism for the formation of the mononuclear perthiocarboxylate complex

In this study it is unclear how the sulfur inserted ligand was formed under mild conditions, and in the absence of an oxidant. Studies involving the mechanism of the sulfur insertion process using labeled ^{34}S revealed that the sulfur atom is inserted between a C-S bond and not between a M-S bond[43,47]. Based on this a mechanism, insertion of a sulfur atom from one dithiocarboxylate molecule into a second one, to form perthiocarboxylate is presented in Scheme 2.5. It was previously noted that the temperature plays an important role for the transformation of a dithiocarboxylate to a perthiocarboxylate ligand, and in this study it can be assumed that the thiophene facilitated the sulfur inclusion under the mild reaction conditions. This could be achieved by the stabilization of the electrophilic CS_2-carbon in the intermediate by electron charge transfer from the thiophene ring. A further driving force is the greater stability of five-membered chelate rings compared to four-membered chelate rings. In conclusion, the

structures of the deep blue compounds **1a**, **2a** and **6a** and the violet compounds **1b**-**6b** are as shown in Figure 2.10.



1a,2a,6a deep blue complexes **1b-6b** violet complexes

Figure 2.10 Structures of nickel(II) dithiocarboxylate complexes

Characterization of complexes:

The mass peak at m/z-value of 632 (^{58}Ni, 3%) corresponds to the mass of the molecule **3b** and represents the molecular ion, $[Ni(S_3CTR)(S_2CTR)]^+$ (R = C_8H_{17}). This can be seen as part of the isotope cluster indicated by a m/z-value of 633 in Figure 2.11 and confirm the assignments of **1b-6b**.

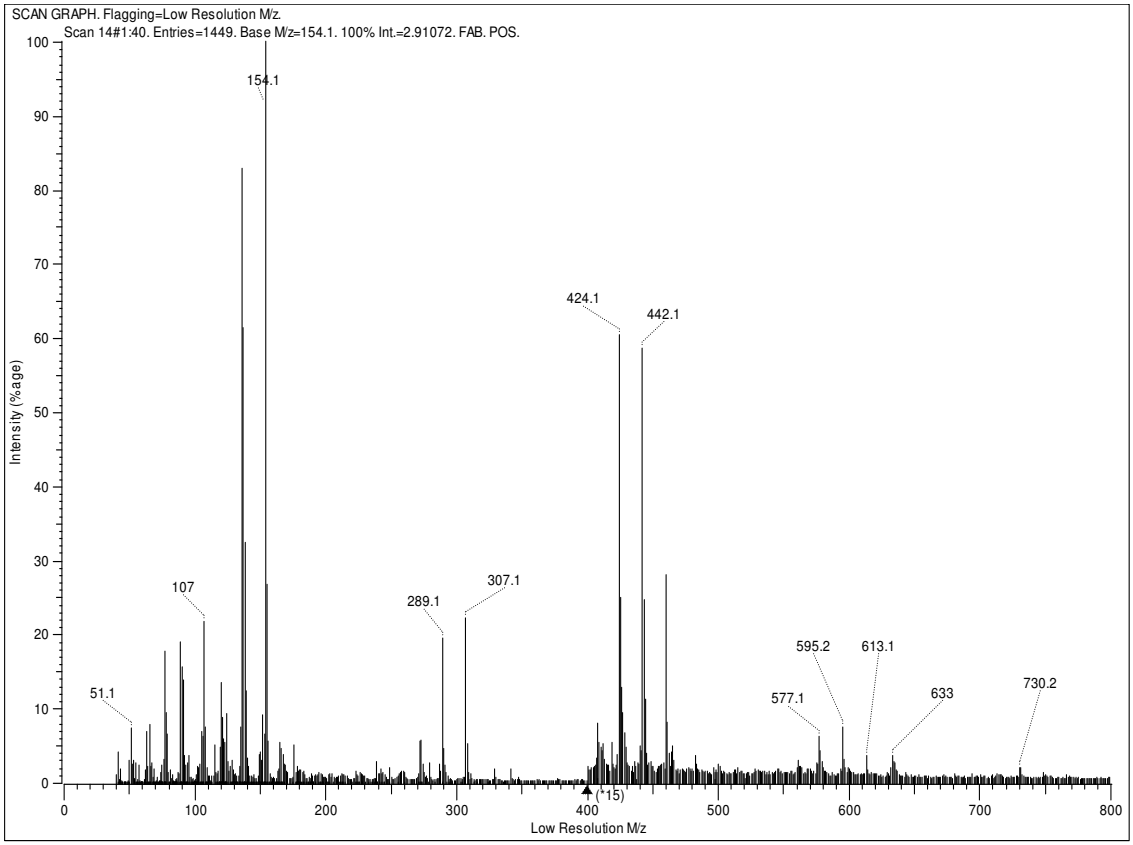


Figure 2.11 Mass spectrum of $[Ni(S_3CTC_8H_{17})(S_2CTC_8H_{17})]^+$**(3b)**

The stronger peaks in the ^1H NMR spectrum of bis(5-butyl-2-thiophenedithiocarboxylato)nickel(II), **1** (Figure 2.1) are two doublets, at chemical shift values of 7.73 and 6.83 ppm for the two protons H3 and H4 of the thiophene ring. The doublet at 7.73 ppm was assigned to H3 that is closer to the dithiocarboxylate (C1) substituent and affected more by the coordination of the sulfur atoms to the nickel. The signal of H3 is expected to be downfield because of the electron withdrawing nature of the dithiocarboxylate group compared to the doublet at 6.83 ppm assigned to H4 because of the alkyl chain in the 5-position.

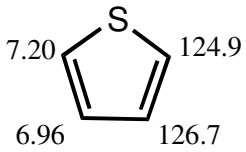


Figure 2.12 ^{1}H and ^{13}C NMR data (δ, ppm) for thiophene[48]

The value for H3 is significantly downfield from the corresponding value of thiophene. Figure 2.12 gives the ^{1}H and ^{13}C NMR chemical shifts for thiophene[48]. The reason for this large downfield shift of almost 1 ppm is the result of the electron-withdrawing CS_2-substituent that is further enhanced as a result of its coordination to the nickel(II) centre. The transfer of electron density from the thiophene ring to the nickel(II) center and the resulting deshielding of H3 is shown in Figure 2.13. The environment of H4 is less affected and this resonance is only marginally upfield because of the inductive effect of the alkyl chain.

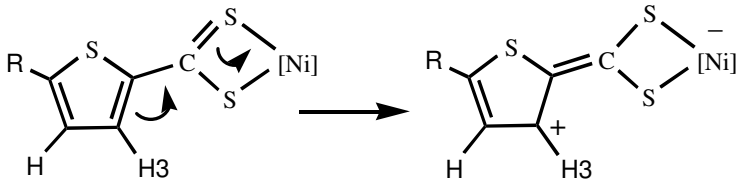


Figure 2.13 Charge delocalization from the thiophene ring to the nickel(II) center

The ^{1}H NMR spectrum of $[Ni(S_2CTC_6H_{13})_2]$ **2a** showed similar peaks to that of $[Ni(S_2CTC_4H_9)_2]$ **1a** and were assigned similarly.

Figure 2.1 shows the ^{1}H NMR spectrum in the thiophene region of **1** (**1a** and **1b**), pure samples of $[Ni(S_2CTR)_2]$ **1a** and $[Ni(S_3CTR)(S_2CTR)]$ **1b** (T = 2,5-disubstituted thiophene, R = C_4H_9) confirmed that this spectrum represents a mixture of the two compounds. The four doublets in the thiophene region of **1b**

support the structure of two different chemical environments for the thiophene-containing ligands. The chemical shifts were assigned based on the resonances observed for the monomer. Instead of the doublet at 7.73 ppm for the monomer **1a**, two doublets were formed, one slightly downfield at 7.78 ppm and the other one slightly upfield at 7.48 ppm. The latter was assigned to H3' of the perthiocarboxylate chelate ring as the introduction of an additional sulfur atom would weaken the effect of coordination to the metal. The other two doublets were at 6.86 ppm slightly downfield, and at 6.75 ppm, slightly upfield from the doublet of the monomer **1a** at 6.83 ppm, and were assigned to H4 and H4', respectively. The phenyl protons of the two types of ligands in $[Ni(S_3CPh)(S_2CPh)]$[43] also gave different chemical shifts and support the structural assignment of **1b.**

The ^{1}H NMR data of **1a**, **1b**, **2a**, **2b**, **3-5b**, **6a** and **6b** are given in Table 2.1. The ^{1}H NMR spectrum of **3b** is shown in Figure 2.14. The four doublets are at 7.77, 7.49, 6.86 and 6.75 ppm, respectively. Interestingly, the triplet of the CH_2 group attached to the thiophene of the octyl chain is also duplicated for the two types of ligands emphasizing the large differences in the coordination modes of the perthio- and dithio-carboxylato ligands.

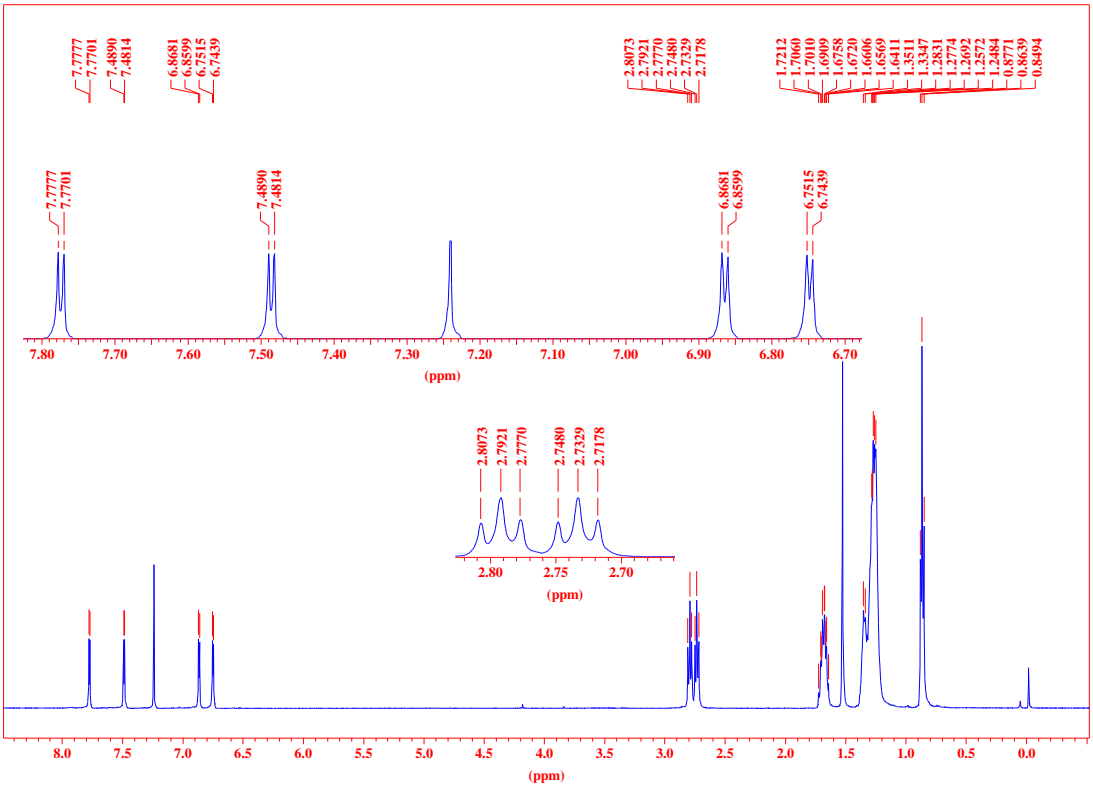


Figure 2.14 ^{1}H NMR spectrum of [Ni($S_3CTC_8H_{17}$)($S_2CTC_8H_{17}$)] **3b**

The resonances in the ^{13}C NMR spectra of **1**-**6b** were assigned based on a 2D HETCOR spectrum recorded for **3b.** The ^{13}C NMR spectrum of **3b** (Figure 2.15) showed the reasonances of CS_2 as one peak for **1a**, **2a** and **6a** and two peaks for **1-6b**. The lower chemical shift value was assigned to the CS_2 of the perthiocarboxylato ligand.

These resonances are typically at 228 ppm for identical dithiocarboxylate ligands and at 214 and 227 ppm for the complexes with mixed dithio- and perthiocarboxylate ligands. The thiophene resonances as well as the carbon atoms of the alkyl chain are also duplicated for the two different ligands in **1b** – **6b** and

are unique for both types of complexes. The ^{13}C NMR data of **1-6** is indicated in Table 2.1.

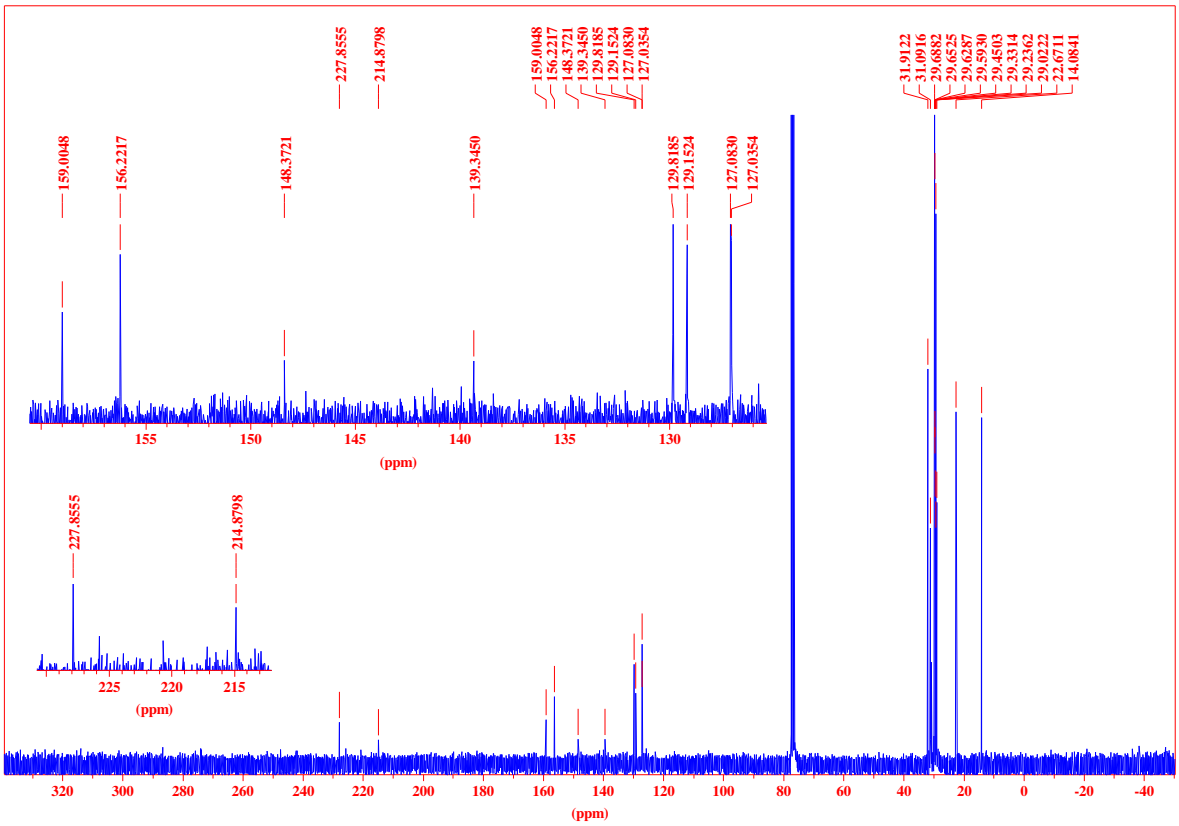


Figure 2.15 ^{13}C NMR spectrum of $[Ni(S_3CTC_8H_{17})(S_2CTC_8H_{17})]$ **3b**

The infrared spectra of all the complexes showed similar peaks. The spectrum of **1a**, $[Ni(S_2CTC_4H_9)_2]$ showed prominent peaks at 2918, 1458, 1375, 1049, 977 and 721 cm^{-1}. The peak at 2918 cm^{-1} was assigned for the CH_2-groups of the alkyl chain and the peak at 1458 cm^{-1} was assigned for the arene-carbon (C-C thiophene) stretching frequency. The peak at 1375 cm^{-1} was assigned for the terminal CH_3 group. The peaks at 1049 and 977 cm^{-1} were assigned for C-S stretching frequencies. Usually the stretching frequencies of the dithiocarboxylic

acid are around 1100 and 900 cm^{-1} for the C=S and C-S stretching frequencies[49,50], respectively and the Ni-S vibrations are found in the far infrared region around 350 cm^{-1} in nickel complexes[51]. The infrared spectral data for the complexes **1-6** is indicated in Table 2.1 and UV spectra of **1a** and **1b** are given in Figure 2.16.

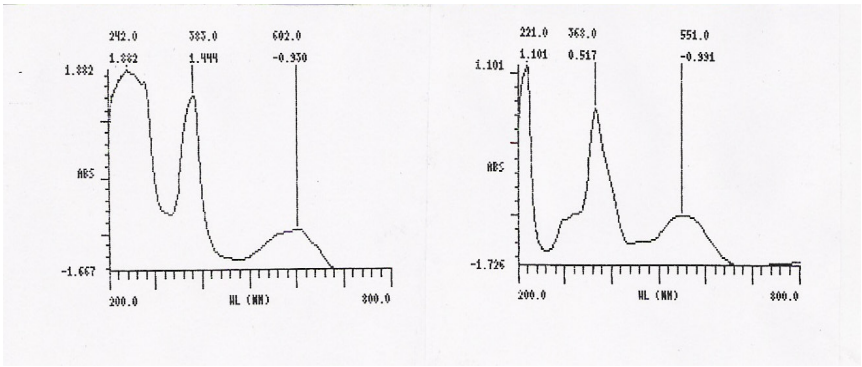


Figure 2.16 UV spectra of **1a** (blue) and **1b** (violet)

The d-d transition of nickel(II) in the blue complex is at 602 nm and the value is similar to that reported by Furlani[52] for monomeric dithiocarboxylate complexes of nickel(II). The d-d transition of nickel(II) in the violet complex is at 551 nm and is similar to that for a mixed dithiobenzoato and perthiobenzoato nickel(II) complex[19].

Chemical analysis of **3b** $Ni(S_2CTC_8H_{17})(S_3CTC_8H_{17})$ for molecular formula $NiC_{26}H_{38}S_7$, showed that the calculated values correspond to the found values. Theoretical values: C = 49.28%, H = 6.05% and S = 35.42%, Analytical values: C = 49.67%, H = 6.25% and S = 37.17%,

Table 2.1 Spectroscopic data of the complexes **1-6**

Complex	^{1}H NMR (δ/ppm in $CDCl_3$)	^{13}C NMR (δ/ppm in $CDCl_3$)	IR (ν/cm^{-1} in Nujol mol)
1a, R = C_4H_9	7.73 (d, 2H, H3, J=3.9), 6.83 (d, 2H, H4, J=3.6), 2.79 (t, 4H, H6, J=7.2), 1.66 (m, 4H, H7), 1.37 (m, 4H, H8), 0.92 (t, 6H, H9, J=7.2)	*S_2C (C1), 159.3 (C2), 148.8 (C5), 129,8 (C3), 127.0 (C4), 33.1, 30.8, 22.7, 13.6 (C6-C9)	2918 (vs), 1458 (vs), 1375 (s), 1049 (m), 977 (m), 721 (s)
1b	7.78 (d, 2H, H3, J=3.9), 7.49 (d, 2H, H3', J=4.1), 6.87 (d, 2H, H4, J=3.9), 6.75 (d, 2H, H4', J=3.9), 2.80 (t, 4H, H6, J=7.2), 2.74 (t, 4H, H6', J=7.2), 1.67 (q, 4H, H7, J=7.5'), 1.66 (q, 4H, H7', J=7.5), 1.40 (m, 4H, H8, J=7.4), 1.39 (m, 4H, H8', J=7.4), 0.93 (t, 6H, H9, J=7.2), 0.92 (t, 6H, H9', J=7.2)	227.9, 214.9 (C1 and C1'), 160.1, 158.2, 149.4, 148.6, 131.3, 129.8, 127.6, 127.2 (C2-C5 and C2'-C5'), 33.6, 31.4, 22.6, 13.9 (C6-C9 and C6`-C9`)	2921 (vs), 1461 (vs), 1375 (s), 1049 (m), 970 (m), 925 (w), 721 (s)
2a, R = C_6H_{13}	7.72 (d, 2H, H3, J=4.1), 6.82 (d, 2H, H4, J=3.9), 2.78 (t, 4H, H6, J=7.7), 1.68 (m, 4H, H7), 1.30 (m, 12H, H8-H10), 0.87 (t, 6H, H11, J=7.5)	*S_2C (C1), 159.4 (C2), 148.8 (C5), 129.6 (C3), 127.0 (C4), 31.4, 31.2, 29.7, 28.7, 22.5, 14.0 (C6-C11)	2920 (s), 1461 (vs), 1375 (s), 1050 (m), 978 (m), 721 (s)
2b	7.77 (d, 2H, H3, J=3.2), 7.48 (d, 2H, H3', J=3.2), 6.86 (d, 2H, H4, J=3.1), 6.75 (d, 2H, H4', J=3.1), 2.82 (dt, 8H, H6 and H6', J=7.2), 1.71 (m, 8H, H7 and H7'), 1.32 (m, 24H, H8-H10 and H8'-H10'), 0.91 (t, 12H, H11 and H11', J=7.2)	227.8, 214.8 (C1 and C1'), 159.0, 156.2, 147.4, 144.6, 139.3, 128.8, 127.1, 127.0 (C2-C5 and C2'-C5'), 30.8, 29.9, 28.9, 27.9, 21.6, 13.1 (C6-C11 and C6'-C11')	2920 (vs), 1460 (vs), 1375 (s), 1097 (m), 1050 (m) 978 (m), 720 (s)
3b, R = C_8H_{17}	7.77 (d, 2H, H3, J=4,0),	227.8, 214.8 (C1 and	2920 (vs),

	7.49 (d, 2H, H3', J=3.7), 6.86 (d, 2H, H4, J=3.8), 6.75 (d, 2H, H4', J=3.8), 2.79 (t, 4H, H6 , J=7.8), 2.74 (t, 8H, H6', J=7.2), 1.67 (m, 8H, H7 and H7`), 1.62 (m, 40H, H8-H12 and H8'-H12'), 0.87 (t, 12H, H13 and H13', J=6.5/7.2')	C1`), 159.0 , 156.2 (C2 and C2'), 148.4, 139.3 (C5 and C5'), 129.8, 129.1 (C3 and C5'), 127.1, 127.0 (C4 and C4'), 31.8, 31.1, 30.7, 29.7, 29.2, 29.0, 22.6, 14.1 (C6-C13 and C6'-C13')	1461 (vs), 1375 (s), 1067 (w), 1048 (m), 999 (m), 970 (m), 721 (s)
4b, R = $C_{12}H_{25}$	7.78 (d, 2H, H3, J=4.0), 7.48 (d, 2H, H3', J=3.9), 6.86 (d, 2H, H4, J=3.9), 6.75 (d, 2H, H4', J=3.9), 2.79 (t, 4H, H6, J=7.6), 2.73 (t, 4H, H6', J=7.5), 1.67 (m, 8H, H7 and H7`), 1.29 (m, 72H, H8-H16 and H8'-H16'), 0.87 (t, 12H, H17 and H17', J=7.2)	227.8, 214.8 (C1 and C1`), 159.0, 156.2, 148.4, 139.3, 129.8, 129.2, 127.1, 127.0 (C2-C5 and C2'-C5'), 31.9, 31.8, 31.4, 31.1, 30.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 29.0, 22.7, 14.1 (C6-C17 and C6'-C17')	2921 (vs), 1460 (vs), 1375 (s), 1049 (m), 994 (w), 980 (m), 720 (s)
5b, R = $C_{16}H_{33}$	7.70 (d, 2H, H3, J=3.9), 7.48 (d, 2H, H3', J=3.9), 6.86 (d, 2H, H4, J=3.9), 6.75 (d, 2H, H4', J=3.9), 2.76 (dt, 8H, H6 and H6', J=7.8/7.5), 1.69 (m, 8H, H7 and H7'), 1.28 (m, 104H, H8-H20 and H8'-H20'), 0.86 (t, H21 and H21', J=6.5/7.0)	227.9, 214.9 (C1 and C1`), 159.0, 156.2, 139.3, 129.8, 129.2, 127.1, 127.0 (C2-C5 and C2'-C5'), 31.9, 31.1, 31.0, 30.7, 30.6, 30.2, 29.9, 29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.2, 29.0, 22.7, 14.1 (C6-C21 and C6'-C21')	2922 (vs), 1458 (vs), 1375 (s), 1049 (m) 977 (m), 925 (w), 720 (s)
6a, R = CH_3	7.72 (d, 2H, H3, J=4.0), 6.82 (d, 2H, H4, J=3.9), 2.43 (s, 3H, Me)	228.0 (C1), 159.0, 139.3, 129.2, 127.1, (C2-C5), 14.1 (C6)	2919 (vs), 1460 (vs), 1375 (s), 1049 (m), 978 (m), 721 (s)
6b, R = CH_3	7.76 (d, 2H, H3, J=3.8),	227.9, 214.9 (C1 and	2920 (vs),

	7.47 (d, 2H, H3', J=3.6), 6.85 (d, 2H, H4, J=3.7), 6.74 (d, 2H, H4', J=3.6), 2.47 (s, 3H, Me), 2.43 (s, 3H, Me')	C1`), 159.0, 156.2, 140.1, 139.3, 129.8, 129.2, 127.1, 127.0 (C2-C5 and C2'-C5'), 14.2, 14.1 (C6 and C6`)	1458 (vs), 1375 (s) 1046 (m), 999 (w), 978 (m), 721 (s)

* not observed.

2.2.2 Thermal properties

Thermal properties of the complexes were investigated by using Differential Scanning Calorimetry (DSC) and Hot-stage Polarising Optical microscopy (POM).

All the complexes were subjected to thermal analysis by DSC. The scanning rate was 10^{o}C per minute. No double melting behaviour was observed for **1a, 1b**, **2a, 2b** and **5b** whereas double melting behaviour was observed for **3b** and **4b**. Two endothermic peaks could be observed at 77^{o}C and 88^{o}C for **3b** (Figure 2.17). The peak at 88^{o}C is compatible with the melting point and the peak at 77^{o}C is for crystal-to-crystal transition. The clearing point was not observed in the DSC. Complex **4b** also showed two endothermic peaks at 102^{o}C and 117^{o}C. Ohta and coworkers[53] suggested that the double melting behaviour of long-chain substituted compounds is a thermal behaviour close to mesomorphism.

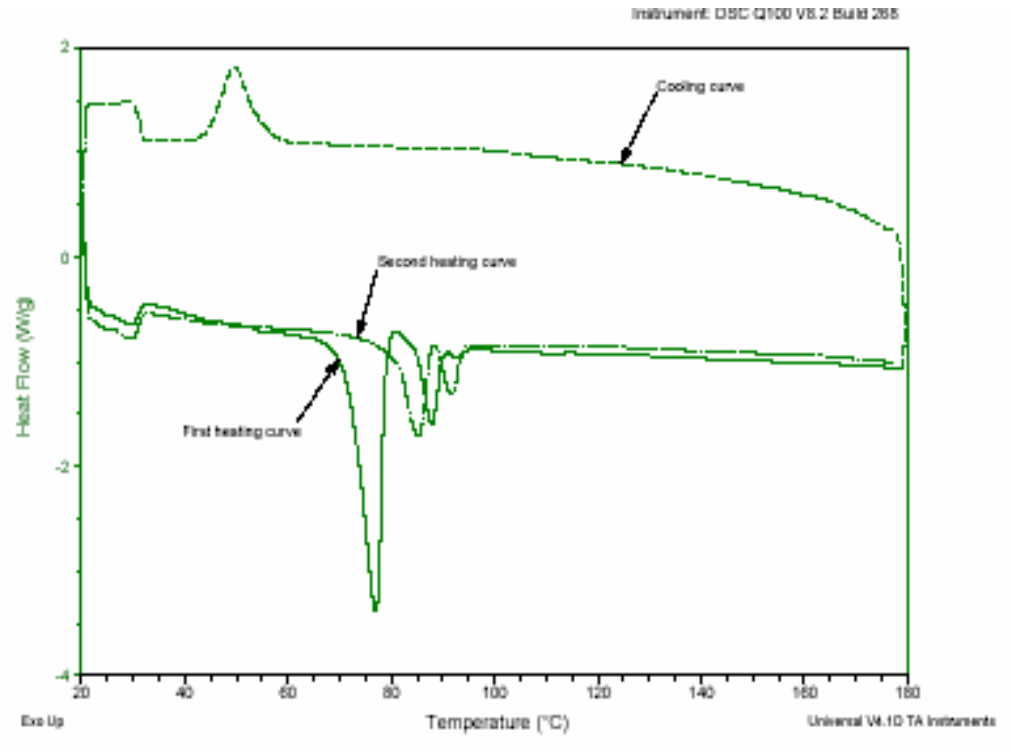


Figure 2.17 DSC thermogram of [Ni($S_3CTC_8H_{17}$)($S_2CTC_8H_{17}$)] **3b**

Complexes **3b**, **4b** and **5b** were also examined by Hot-stage Polarising Optical Microscopy. The complex **3b** (Figure 2.18) is an enantiotropic liquid crystal and it exhibits a nematic phase. Enantiotropic liquid crystal shows mesomorphism upon heating the solid as well as on cooling the isotropic liquid. The transition temperature of **3b** was between 92°C and 116°C.

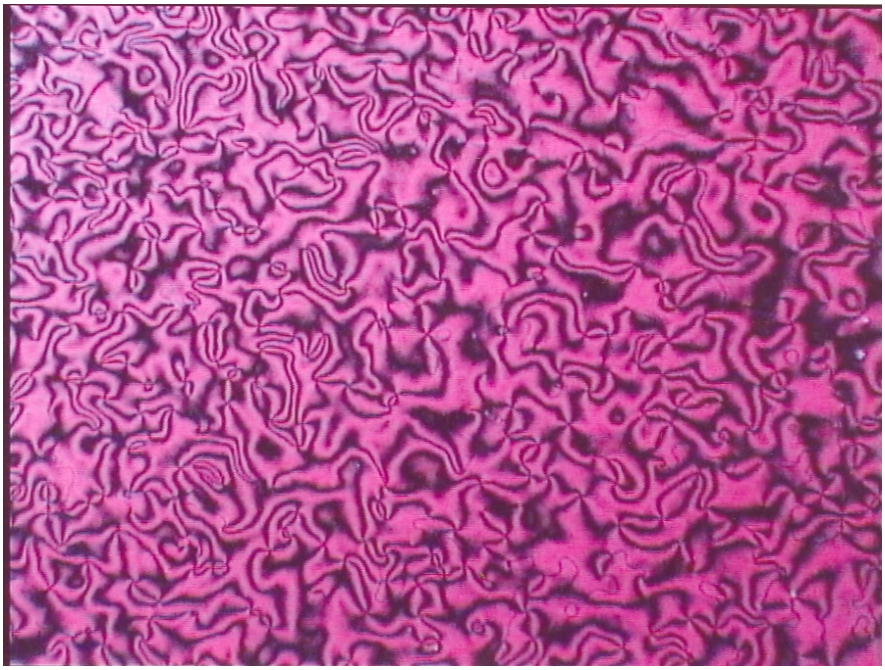


Figure 2.18 Nematic phase of [Ni($S_3CTC_8H_{17}$)($S_2CTC_8H_{17}$)] **3b** at 105°C (200 x magnification)

The optical texture of **3b** is similar to the nematic phase of 4-nonyloxybenzoic acid[54] described in chapter 1. Complex **4b** was a mixture of dark highly viscous liquid and opaque crystals. The liquid was not birefringent and therefore it was not a liquid crystal. The opaque crystals however melted to a nematic phase, but it was difficult to observe because of the presence of the other dark fluid phase. Complex **5b** directly melted to isotropic liquid without showing any mesophases. Transition temperatures of the complexes **1-5** are given in Table 2.2, and the dependence of the transition temperatures on the chain length is shown in Figure 2.19.

Table 2.2 Transition temperatures of **1-5**

Complex	Chain	Transition	Temperature (^{o}C)
1a	C_4H_9	$Cr \rightarrow I$	52
2a	C_6H_{13}	$Cr \rightarrow I$	65
3b	C_8H_{17}	$Cr \rightarrow N$ $N \rightarrow I$	92 116
4b	$C_{12}H_{25}$	$Cr \rightarrow N$ $N \rightarrow I$	102 117
5b	$C_{16}H_{33}$	$Cr \rightarrow I$	61

Cr = crystal, *N* = nematic phase, *I* = isotropic liquid

Complexes **1, 2** and **5b** directly melted to the isotropic liquids without passing through any mesophases. The transition temperature range for **3b** was between 92^{o}C-116^{o}C (*N*→*I*) whereas for benzene analogue[18] [Ni($S_3CBC_8H_{17}$)($S_2CBC_8H_{17}$), the range was between 126^{o}C-198^{o}C (*N*→*I*). The lower transition temperature observed for **3b** may be due to thiophene in the complex. It was reported[55] that thiophene systems have generally lower melting points than their benzene counter parts due to reduced packing efficiency in the molecules.

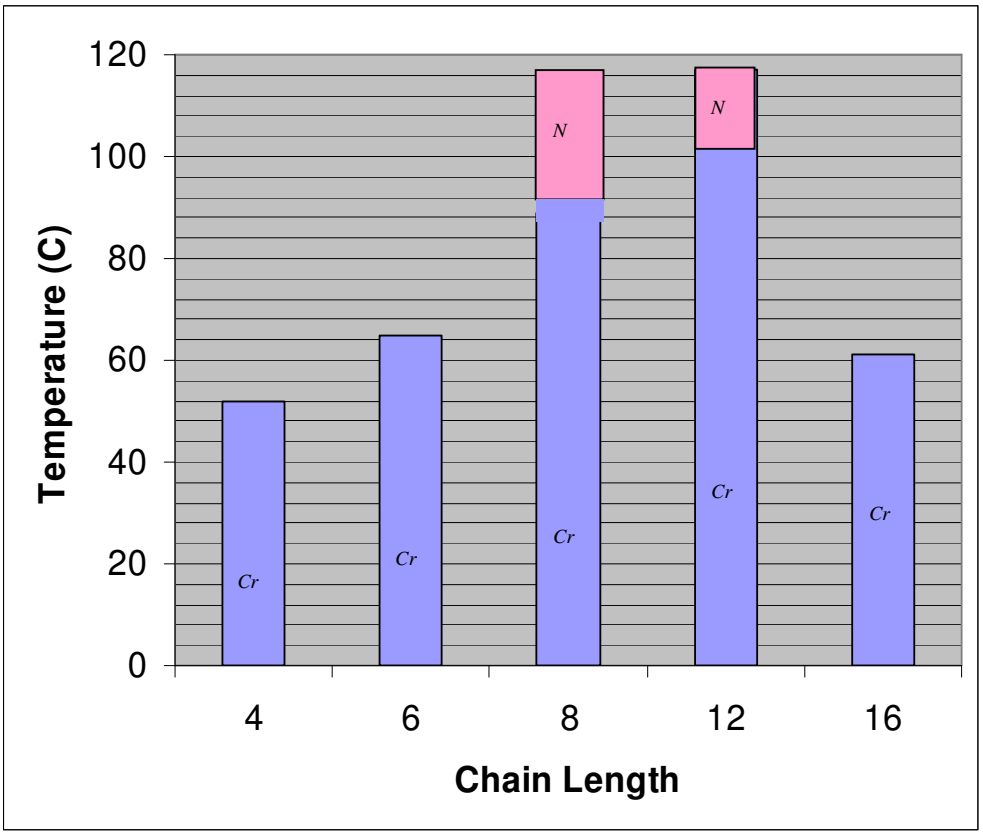


Figure 2.19 The dependence of the transition temperatures of the complexes on the alkyl chain length *(N = nematic , Cr = crystal)*

Complexes **1a, 1b, 2a, 2b** and **5b** had no mesogenic behaviour whereas complexes **3b** and **4b** showed nematic mesophases. The optimum chain length suitable for mesomorphism for the alkyl thiophene dithiocarboxylate complexes was C_8.

2.3 Experimental Section

Materials and instrumentation

All commercially available chemicals were used as received. Solvents were dried and distilled under nitrogen prior to use. Thiophene was purified as described by Spies and Angelici[56]. All reactions were performed in an inert atmosphere of either nitrogen or argon by using Schlenk techniques and vacuum-line. Column chromatography was carried out using silica gel.

Infrared spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectrophotometer. All NMR spectra were recorded in deuterated chloroform using the chloroform peak as standard on a Bruker ARX – 300 spectrometer. High-resolution mass spectra were recorded on a Finnegan 8200 spectrometer. UV- visible spectra were recorded on a Varian Cary 1E spectrometer.

Liquid-crystalline properties were examined on a Differential Scanning Calorimeter (DSC) Q 100 V8.2 Build 268 and Hot-stage Polarising Optical Microscope (POM) Olympus BX60 equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 Programmable temperature controller.

2.3.1 Synthesis

All the complexes were synthesized via a four-step reaction in a similar manner. A typical procedure for complex **1** is described.

Preparation of 2-butyl thiophene

The reaction was done in an inert atmosphere. The procedure which was used is similar to the one described by Brandsma[23]. n-Butyl lithium (15.6 ml, 25.0 mmol) was added to a mixture of THF (50.0 ml) and hexane (30.0 ml), which was cooled to -20°C. Thiophene (1.68 g, 20.0 mmol) was introduced over 10 minutes with cooling between 0°C and 10°C. The cooling bath was removed and allowed to rise to the room temperature. Butyl bromide (2.74 g, 20.0 mmol) was added in one portion without external cooling. The temperature of the solution was raised to 50°C and kept at this temperature for a further 30 minutes and after which 100 ml of ice water was added with vigorous stirring. Two separate layers were observed and the separation was done in air. After separation of the layers, two extractions with diethyl ether were carried out. The combined organic solutions were dried over anhydrous $MgSO_4$ and concentrated in a rotary evaporator and weighed. Yield = 2.38 g; 85%.

Preparation of 5-butyl-2-thiophenedithiocarboxylic acid ($C_4H_9TCS_2H$)

In the second step 2-butyl thiophene was converted into 5-butyl-2-thiophenedithiocarboxylic acid. The first part of the reaction was done in an inert atmosphere. n-Butyl lithium (12.5 ml, 20.0 mmol) was added to a solution of THF (50.0ml) and hexane (30.0 ml), which was cooled to -20°C. 2-butyl thiophene (2.38 g, 17.0 mmol) was introduced over 10 minutes with cooling between 0°C and 10°C. The cooling bath was removed and allowed to rise to room temperature and stirred for a further 10 minutes. The solution was cooled to 0°C and copper(I) bromide (0.1 g) was added. Carbon disulfide (1.29 g, 17.0

mmol) was added drop-wise to the stirred mixture. The colour of the reaction mixture changed to a deep-red colour. The cooling bath was removed and allowed to rise to the room temperature and stirring was continued for a further 1 hour. Ice water (100.0 ml) was added followed by dilute hydrochloric acid (20.0 ml, 1mol/dm^3). The next part was done in air. The organic layer was separated and extracted into diethyl ether (70.0 ml) and washed with 2 x 50.0 ml of water. The product was dried over $MgSO_4$ and the solvent removed *in vacuo*. Yield = 3.30 g; 89.8%.

Preparation of sodium-5-butyl-2-thiophenedithocarboxylate ($C_4H_9TCS_2Na$)

The reaction was done in an inert atmosphere. Sodium metal (0.35 g, 15.28 mmol) was added over 10 minutes to vigorously stirred methanol (50.0 ml). When all the sodium had dissolved, additional (20.0 ml) methanol was added. 5-Butyl-2-thiophenedithiocarboxylic acid (3.30 g, 15.28 mmol) was added over 5 minutes to the mixture and left stirring for 30 minutes. The solvent was removed *in vacuo*, leaving the sodium 5-butyl-2-thiophenedithiocarboxylate as an orange-brown solid. Yield = 3.09 g; 85%.

*Synthesis of Bis(5-butyl-2-thiophenedithiocarboxylato) nickel(II) [$Ni(S_2CTC_4H_9)_2$] (**1a**)*

The procedure was similar to that of Adams *et al.*[18], who prepared dithiobenzoate complexes. The reaction was done in air. To a stirred solution of sodium 5-butyl-2-thiophenedithiocarboxylate (1.55 g, 6.5 mmol) in water (25.0 ml) was added drop-wise a pale green solution of $NiCl_2.6H_2O$ (0.71 g, 3.0 mmol) in water (10.0

ml) at room temperature. The colour of the solution turned blue-violet and the mixture was left to stir for 3 hours. The mixture was concentrated to 25.0 ml on a rotary evaporator and 20.0 ml of methanol was added. The precipitate was separated by filtration and dried. The product was purified on a silica gel column and the desired product was extracted with hexane: CH_2Cl_2 (4:1) as the eluent. A blue powder was obtained on evaporation of the solvent. Yield = 0.49 g; 66%.

The synthetic route for the other four complexes was similar. The experimental data of the complexes **1-5** are summarized in Table 2.3.

Table 2.3 The experimental data of **1-5**

Complex	Amount of nickel(II) chloride added (mmol)	Amount of sodium salt (mmol)	Colour of the product	Yield (%)
1a	3.0	6.5	Dark blue solid	66
2a	2.0	5.0	Dark blue solid	58
3b	2.5	5.8	Violet powder	64
4b	2.2	5.0	Dark violet oily solid	48
5b	1.8	4.0	Dark violet oily solid	52

*Second method (one-pot reaction) for **6a** and **6b***

In a second method (one-pot reaction), 2-methylthiophene (1.96 g, 20.0 mmol) was lithiated by n-butyl lithium (13.8 ml, 22.0 mmol) at –20°C in THF. The

colour of the solution immediately changed to orange on addition of the BuLi, but changed gradually to yellow after stirring for 30 minutes. The mixture was cooled to -50° and carbon disulfide (1.52 g, 20.0 mmol) was added. The mixture became dark red in colour and was stirred for 30 minutes. Anhydrous nickel(II) chloride (1.30 g, 10.0 mmol) was added in small portions and the mixture was allowed to reach room temperature. The yellow solid material gradually dissolved on reacting and the solution changed first to green then to blue and thereafter to violet over a period of three hours. The blue-violet product was purified by filtration of the reaction mixture through a plug of silica gel once the solvent was changed to dichloromethane and afforded **6** in very high yield (the yield was more than 80%). From this mixture both blue and violet compounds were isolated by column chromatography with mixtures of hexane and dichloromethane as eluents.

Yield of **6a** (blue) = 1.22 g, 30%.

Yield of **6b** (violet) = 1.63 g, 40%.

2.4 Conclusion

The reactions of a series of 5-alkyl-2-thiophenedithiocarboxylates with nickel(II) chloride formed two types of complexes, mononuclear nickel(II) complexes with two terminal dithiocarboxylate ligands (blue) and mononuclear nickel(II) complexes with perthio- and dithiocarboxylate ligands (violet). The formation of violet vs blue compounds in this study was contributed not only by the properties of the solvent, but also by the length of the alkyl chain and the presence of thiophene in the chain. Using the first method of synthesis the blue monomers are preferred for the shorter chains (C_4 and C_6) and violet compounds for the longer

chains (C_8, C_{12} and C_{16}). It was previously noted[19] that the temperature plays an important role for the transformation of dithiocarboxylate to a perthiocarboxylate ligand. In this study it can be assumed that the thiophene facilitated the sulfur inclusion under the mild reaction conditions. The blue compounds are less soluble than the violet compounds. Thermal studies with DSC and POM showed that the complexes with C_8 and C_{12} alkyl chains are liquid crystals (metallomesogens). The mesomorphism of the two complexes was similar, as both complexes showed nematic phases. The dark colour of the complexes has made phase characterization very difficult. The transition temperatures of these complexes are lower than the benzene analogues[18] as predicted. Complexes **3b** and **4b** are the first examples of metallomesogens of nickel(II) complexes with 5-alkyl-2-thiophenedithiocarboxylate as ligands. In future, further work will be done on the optical and conducting properties of these complexes.

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