

Synthesis and thermal behaviour of cyclopentadienylnickel(II) thiolato Schiff base complexes. Molecular structures of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBU}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{C}_6\text{H}_5)$ and $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBU}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OC}_4\text{H}_9)$

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Abstract

The new complexes $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})$, $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{C}_6\text{H}_5)$ and $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{NC}(\text{H})\text{C}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_5)$, ($\text{R} = \text{Ph}$ or Bu ; $n = 4, 6, 8, 10, 14, 16$ and 20), were synthesised from equimolar amounts of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)\text{Br}$ ($\text{R} = \text{Ph}$ or Bu) and the appropriate thiol ligand and were characterised by NMR and elemental analysis. In addition **1a** and **3a** were characterised by single crystal X-ray diffraction studies. These new complexes were also examined by thermal analytical methods (DSC and TGA) and polarising hot-stage microscopy, but were not found to exhibit any liquid crystalline behaviour. Thermal analysis showed that the complexes were generally stable up to about 180 °C and decomposed finally to a species with empirical formula NiSC_6H_5 . Two decomposition pathways were established, depending on the phosphine used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienylnickel(II); Thiolato Schiff base complexes; Thermal behaviour

1. Introduction

The search for metal Schiff base complexes is driven in part by their potential use in material science. Two specific applications are liquid crystals [1] and non-linear optical materials [2]. In most complexes that behave as liquid crystals or exhibit non-linear optical behaviour, the imine group of the Schiff base only forms part of the ligand backbone and is not coordinated to the metal centre. The imine group is thus used as a linker between aromatic rings in both of these applications.

We have recently reported the preparation of nickel complexes that contain Schiff base ligands bound to the metal through a sulfur atom [3]. This was done in an attempt to prepare nickel Schiff base metallomesogens,

using what could be described as a non-conventional approach. The conventional approach involves complexation of an organic liquid crystalline compound with a metal fragment. However, metal complexes thus formed by this conventional route do not always show liquid crystalline properties [4].

In preparing the complexes reported here we have combined features found in two types of metallomesogens. The first type is a Schiff base metal complexes that have the Schiff base directly bound to the metal, with the imine group as part of the ligand backbone, $\text{HgCl}(\text{C}_6\text{H}_4\text{-4-N=CH-C}_6\text{H}_4\text{-4'-OMe})$, $\text{Hg}(\text{C}_6\text{H}_4\text{-4-N=CH-C}_6\text{H}_4\text{-4'-OMe})_2$ [5a] and $\text{M}(\text{CO})_2\text{Cl}(\text{NC}_5\text{H}_5\text{-4-N=CH-C}_6\text{H}_4\text{-4'-C}_n\text{H}_{2n+1})$ ($\text{M} = \text{Rh, Ir}$; $n = 5\text{--}12$) [5a,b]. The second type is metal thiolato complexes that have either monothiolato ligands, $\text{AgSC}_n\text{H}_{2n+1}$ ($n = 4, 6, 8, 10, 12, 16, 18$) [6], or dithiolato ligands, $\text{Ni}_2(\text{S}_2\text{C-C}_n\text{H}_{2n+1})_4$ ($n = 5\text{--}12$) [7], $\text{Ni}(\text{S}_2\text{C-C}_6\text{H}_4\text{-4-OC}_n\text{H}_{2n+1})_2$ ($n = 4, 8$) [8] and $\text{Ni}(\text{S}_3\text{C-C}_6\text{H}_4\text{-4-OC}_n\text{H}_{2n+1})(\text{S}_2\text{C-C}_6\text{H}_4\text{-4-OC}_n\text{H}_{2n+1})$ ($n = 4, 8$) [9]. We

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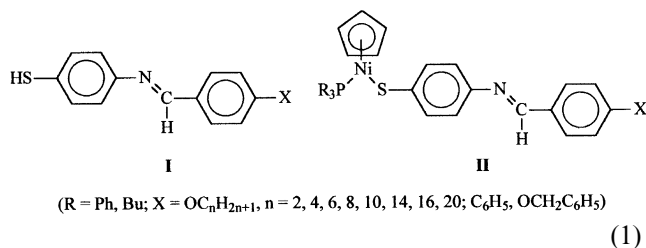
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Table 1

¹H NMR data and elemental analysis for Schiff bases (calculated values in brackets)

Compound	¹ H-NMR	Elemental analysis		
		C	H	N
1	8.48(s), 7.96(d), 7.75(d), 7.64 (m), 7.14(d)	74.68 (75.20)	5.56 (5.36)	4.32 (4.38)
2	8.37(s), 7.83(d), 7.40(m), 7.08(dd), 5.14(s), 3.47(s)	74.92 (74.74)	5.85 (5.33)	4.45 (4.36)
3	8.36(s), 7.82(d), 7.30(d), 7.10(d), 6.97(d), 3.47(s)	71.72 (71.55)	6.43 (6.71)	5.04 (4.91)
4	8.36(s), 7.82(d), 7.52(d), 7.14(d), 6.96(d)	72.86 (72.81)	7.51 (7.39)	4.60 (4.47)
5	8.35(s), 7.84(d), 7.52(d), 7.16(d), 6.97(d)	74.11 (74.08)	7.49 (7.70)	4.23 (4.11)
6	8.35(s), 7.82(d), 7.52(d), 7.15(d), 6.96(d)	73.73 (74.29)	10.08 (9.86)	3.67 (4.15)
7	8.35(s), 7.81(d), 7.51(d), 7.14(d), 6.96(d)	76.55 (76.18)	8.95 (9.23)	3.75 (3.29)
8	8.36(s), 7.82(d), 7.30(d), 7.10(d), 6.96(d), 3.47(s)	76.61 (76.77)	10.77 (9.99)	2.78 (3.09)
9	8.35(s), 7.82(d), 7.51(d), 7.14(d), 6.96(d), 3.47(s)	77.52 (77.74)	9.75 (10.08)	3.33 (2.75)

have thus prepared the Schiff base thiols (**I**) and their nickel complexes (**II**) in an effort to obtain metallo-mesogens. Thermal studies of the ligands and the complexes using differential scanning calorimetry (DSC) and polarising hot-stage microscopy showed that neither the ligands nor the complexes have any mesogenic properties. They, however, show the effect of alkoxy chain length on the thermal behaviour of both the ligands and the complexes, which is reported herein.



2. Experimental

2.1. Materials and instrumentation

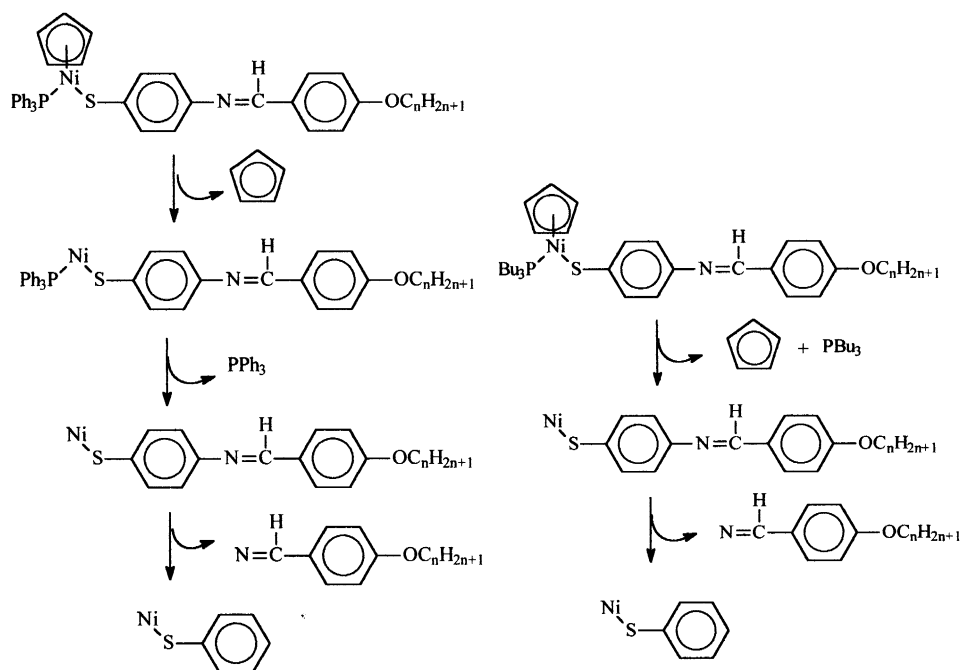
All commercially available chemicals were used as received. The following specialty chemicals were purchased: 4-aminothiophenol (Fluka), 1-bromooctane (Saarchem, South Africa), 4-hydroxybenzaldehyde, 4-biphenylcarboxyaldehyde, 4-benzyloxybenzaldehyde, 4-butyloxybenzaldehyde, 1-bromodecane, 1-bromohexadecane, Et₃N (Aldrich). The nickel compounds Ni(η⁵-C₅H₅)(PPh₃)Br and Ni(η⁵-C₅H₅)(PBU₃)Br were prepared by literature methods [10]. The compounds OHCC₆H₄OR-4 (R = C_nH_{2n+1}, n = 2, 6, 8, 10, 14, 16 and 20) were prepared by a modified literature procedure [11]. The Schiff base compounds were synthesised by the condensation reaction between the aldehydes and 4-aminothiophenol in ethanol as recently reported [3] and characterised by ¹H-NMR, GC-MS and elemental analysis. Reagent grade hexane was distilled and then stored over molecular sieves, while toluene was distilled from sodium. All reactions were performed using standard Schlenk techniques under dinitrogen atmosphere.

IR spectra were obtained on a Perkin-Elmer Paragon 1000 PC FT spectrometer as Nujol mulls. The ¹H- and ³¹P-NMR spectra were acquired on a Varian Gemini 2000 spectrometer at 200 and 80.961 MHz and referenced to residual CHCl₃ (δ 7.26) and externally to PPh₃ (δ – 5.00), respectively. Thermal analyses were performed on a Universal V2.3H TA instrument. Elemental analysis and GC-MS (in electron impact mode) were performed in the Department of Chemistry at the University of the Western Cape.

X-ray diffraction data were collected at a low temperature on a Nonius Kappa CCD with 1.5 kW graphite monochromated Mo radiation. A selection of crystal and refinement data is given in Table 3. The strategy for the data collection was evaluated using the COLLECT software [12]. The data were scaled and reduced using DENZO-SMN [13]. Unit cell dimensions were refined on all data. The data were treated for absorption using the program SORTAV [14]. The structures were solved and refined using SHELX97 [15]. Hydrogen atoms were placed in calculated positions and refined as riding atoms. Molecular graphics and additional material for publication were obtained using the program PLATON [16].

Table 2
Melting points of selected complexes

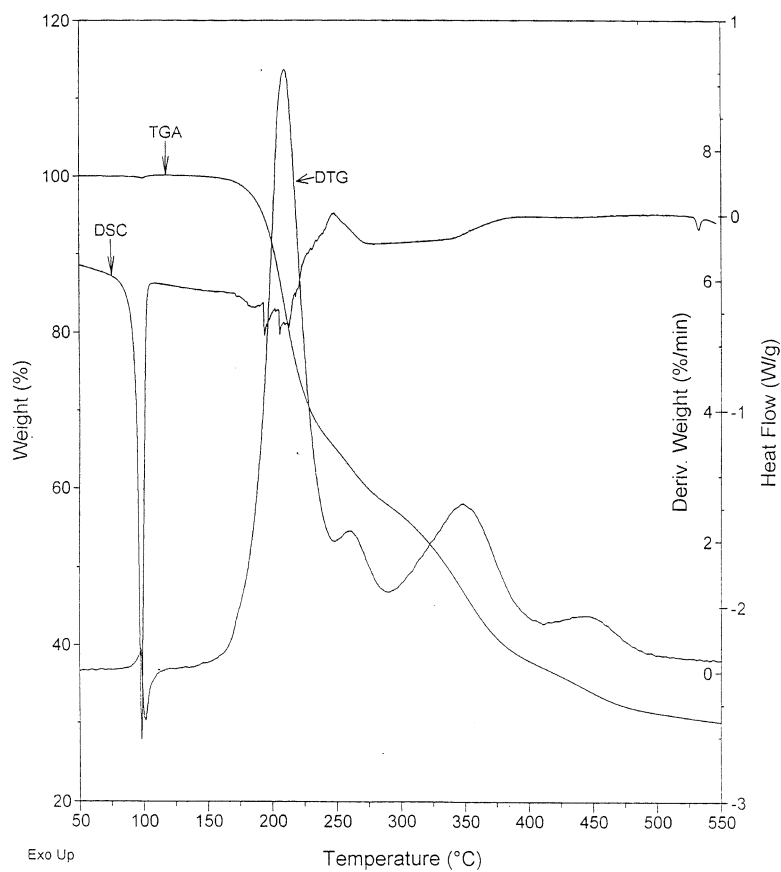
Complex	Melting point (°C)
3a	99.97
3b	138.83
6a	62.24
6b	120.11
7a	52.26
7b	90.21
8b	89.70
9a	49.70
9b	101.77



Scheme 1a

Scheme 1b

Scheme 1. Thermal decomposition patterns of: (a) PPh_3 complexes; and (b) PBu_3 complexes.

Fig. 1. TGA-DSC curves for **3a**.

2.2. $Ni(\eta^5-C_5H_5)(PBU_3)(SC_6H_4NC(H)C_6H_4C_6H_5)$ (**1a**)

Preparation of cyclopentadienylnickel thiolato Schiff base is representative and will only be described in detail for compound **1a**. To a degassed solution of $HSC_6H_4NC(H)C_6H_4C_6H_5$ (0.2 g, 0.63 mmol) and $Ni(\eta^5-C_5H_5)(PBU_3)Br$ (0.28 g, 0.68 mmol) in toluene (50 ml) was added excess Et_3N (1.5 ml). The maroon solution immediately turned to dark green immediately and was stirred at room temperature (r.t.) for 15 h. The

mixture was filtered to remove the white Et_3NHBr by-product and the filtrate evaporated. The residue was recrystallised from hexane at $-15^\circ C$ to give green crystalline product in a yield of 0.12 g (38%). 1H -NMR ($CDCl_3$, δ ppm): 8.52 (s, 1H, $N=C(H)$), 7.94 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4$), 7.67 (m, 5H, NC_6H_4 , C_6H_5), 7.43 (m, 4H, $C(H)C_6H_4$, C_6H_5), 6.99 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.28 (s, 5H, $\eta^5-C_5H_5$), 1.52–1.35 (m, 18H, butyl), 0.92 (t, 9H, CH_3). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, δ ppm): 25.36. Anal. Found: C, 68.78; H, 7.89; N, 2.14. Calc. for $C_{36}H_{46}NPSNi$: C, 69.17; H, 7.53; N, 2.18%

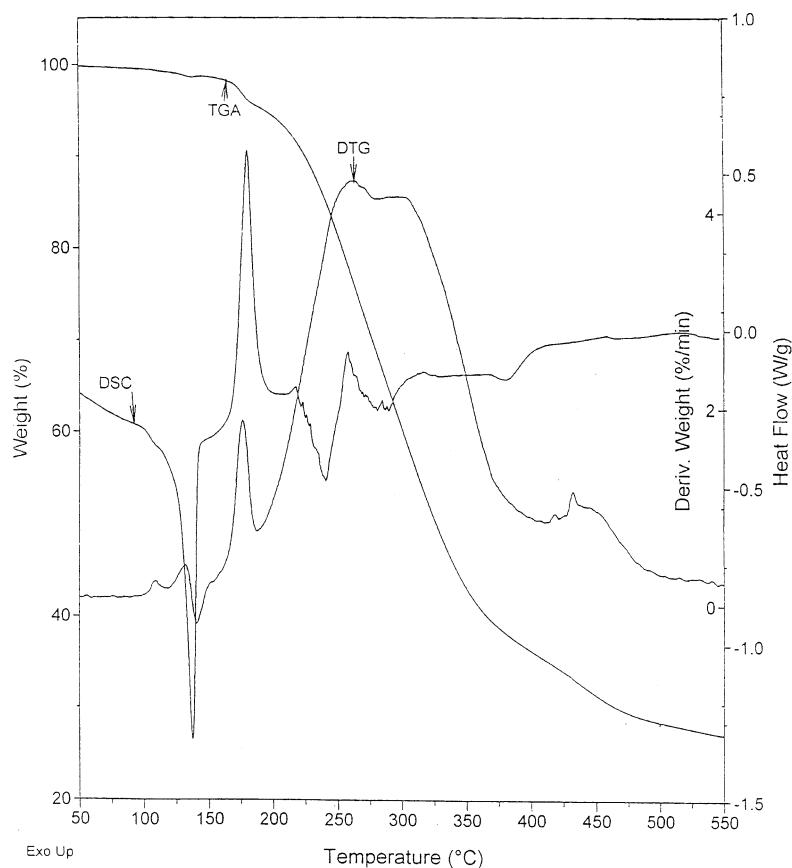


Fig. 2. TGA-DSC curves for **3b**.

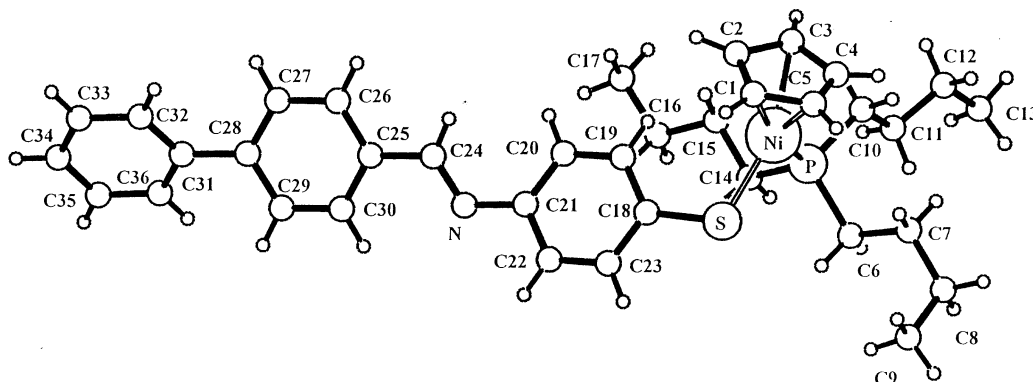
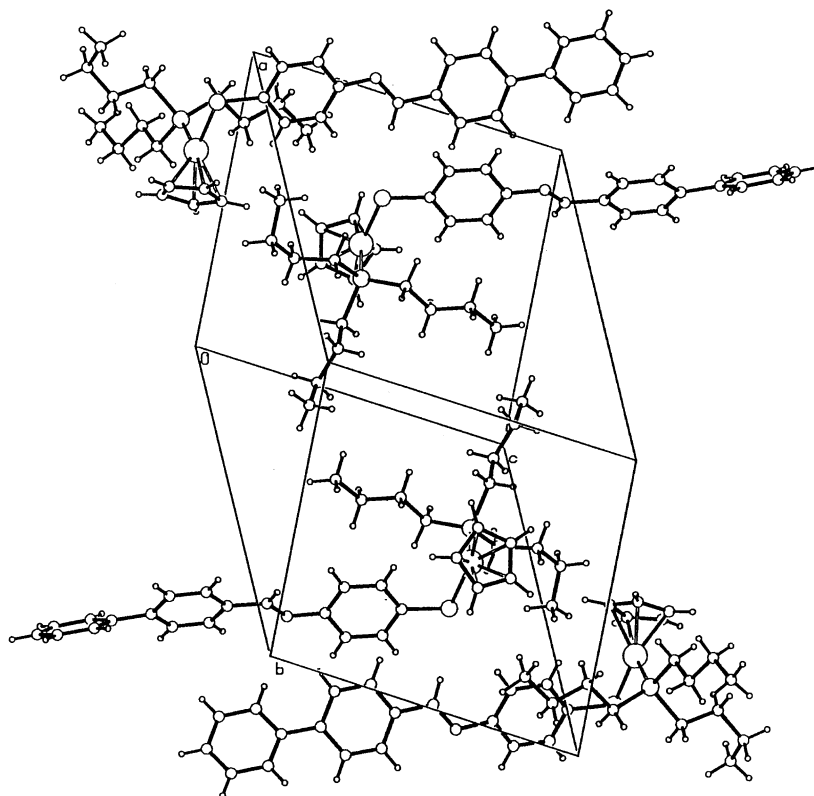


Fig. 3. Molecular structure of **1a**.

Fig. 4. Packing diagram for **1a**.

The synthetic route for the remaining complexes is similar to **1a**.

2.3. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OCH_2C_6H_5)$ (2a**)**

A green solid was obtained with a yield of 0.34 g (33%). 1H -NMR ($CDCl_3$, δ ppm): 8.40 (s, 1H, $N=C(H)$), 7.82 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4$), 7.62 (d, 2H, $J_{HH} = 8.0$ Hz, NC_6H_4), 7.40 (m, 5H, $OCH_2C_6H_5$), 7.04 (d, 2H, $J_{HH} = 8.4$ Hz, OC_6H_4), 6.93 (d, 2H, $J_{HH} = 8.4$ Hz, SC_6H_4), 5.27 (s, 5H, $\eta^5-C_5H_5$), 5.13 (s, 2H, OCH_2), 1.43–1.27 (m, 18H, butyl), 0.92 (t, 9H, CH_3). $^{31}P\{^1H\}$ -NMR (δ ppm): 27.33. Anal. Found: C, 69.22; H, 7.62; N, 2.08. Calc. for $C_{37}H_{48}NOPSNi$: C, 68.95; H, 7.22, N, 2.18%.

2.4. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_4H_9)$ (3a**)**

Green crystals with a yield of 0.94 g (88%) were obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.39 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.61 (d, 2H, $J_{HH} = 8.4$ Hz, NC_6H_4), 6.94 (d, 2H, $J_{HH} = 8.8$ Hz, OC_6H_4), 6.93 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.26 (s, 5H, $\eta^5-C_5H_5$), 4.02 (t, 2H, OCH_2), 1.80 (q, 2H, OCH_2CH_2), 1.41 (m, 20H, alkoxy, butyl), 0.98 (t, 12H, alkoxy, butyl). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, δ ppm): 25.29. Anal. Found: C, 66.82; H, 8.33; N, 2.77. Calc. for $C_{34}H_{50}NOPSNi$: C, 66.89; H, 8.25; N, 2.29%.

2.5. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_6H_{13})$ (4a**)**

A green solid with a yield of 76% (0.58 g) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.39 (s, 1H, $C(H)N$), 7.80 (d, 2H, $J_{HH} = 8.2$ Hz, $C(H)C_6H_4$), 7.60 (d, 2H, $J_{HH} = 8.2$ Hz, NC_6H_4), 6.94 (d, 2H, $J_{HH} = 8.4$ Hz, OC_6H_4), 6.93 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.26 (s, 5H, $\eta^5-C_5H_5$), 4.02 (t, 2H, OCH_2), 1.80–1.25 (m, 26H, alkyl), 0.92 (t, 12H, alkoxy, butyl). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, δ ppm): 25.26. Anal. Found: C, 68.04; H, 8.62; N, 2.40. Calc. for $C_{36}H_{54}NOPSNi$: C, 67.93; H, 8.55; N, 2.20%.

2.6. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_8H_{17})$ (5a**)**

A green solid with a yield of 0.43 g (75%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.39 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4$), 7.60 (d, 2H, $J_{HH} = 8.4$ Hz, NC_6H_4), 6.94 (d, 2H, $J_{HH} = 8.8$ Hz, OC_6H_4), 6.93 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.26 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.80–1.23 (m, 30H, alkoxy, butyl), 0.92 (t, 12H, alkoxy, butyl). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, δ ppm): 25.26. Anal. Found: C, 69.65; H, 8.52; N, 1.69. Calc. for $C_{38}H_{58}NOPSNi$: C, 69.71; H, 8.93; N, 2.14%.

2.7. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_{10}H_{21})$ (**6a**)

A green solid with a yield of 0.26 g (46%) was obtained. 1H NMR ($CDCl_3$, δ ppm): 8.39 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.61 (d, 2H, $J_{HH} = 8.4$ Hz, NC_6H_4), 6.95 (d, 2H, $J_{HH} = 8.8$

Table 3
Crystal data and structure refinement parameters for compounds **1a** and **3a**

	1a	3a
Empirical formula	$C_{34}H_{50}NOPSNi$	$C_{36}H_{46}NPSNi$
Formula weight	610.49	614.48
Temperature (K)	150(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions		
a (Å)	10.455(1)	13.164(2)
b (Å)	12.375(1)	20.277(2)
c (Å)	13.567(1)	12.740(2)
α (°)	104.25(1)	90.0
β (°)	99.31(1)	106.46(1)
γ (°)	92.47(1)	90.0
V (Å ³)	1672.6(2)	3261.2(11)
Z	2	4
D_{calc} (Mg m ⁻³)	1.212	1.252
Absorption coefficient (mm ⁻¹)	0.716	0.733
$F(000)$	656	1312
Crystal size (mm)	$0.35 \times 0.35 \times 0.25$	$0.41 \times 0.37 \times 0.25$
Reflections collected	13 454	12 387
Unique reflections	7614	6623
Completeness to $\theta = 25^\circ$ (%)	99.8	97.9
R_{int}	0.0191	0.0326
Data/restraints/parameters	7614/0/357	6623/0/463
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0338$, $wR_2 = 0.0717$	$R_1 = 0.0409$, $wR_2 = 0.0845$
R indices (all data)	$R_1 = 0.0495$, $wR_2 = 0.0774$	$R_1 = 0.0693$, $wR_2 = 0.0950$
Largest difference peak and hole (e Å ⁻³)	0.332 and −0.353	0.445 and −0.418

Table 4
Selected bond lengths (Å) and bond angles (°) for **1a**

<i>Bond lengths</i>			
Ni–S	2.193(1)	Ni–P	2.145(1)
Ni–Cp ^a	1.750(3)	C(18)–S	1.764(2)
C(24)–N	1.277(3)	C(6)–P	1.828(2)
C(10)–P	1.834(2)	C(14)–P	1.824(2)
<i>Bond angles</i>			
S–Ni–Cp	132.43(1)	P–Ni–Cp	136.28(1)
C(18)–S–Ni	107.5(1)	C(14)–P–Ni	115.1(1)
P–Ni–S	91.7(1)	C(6)–P–Ni	113.6(1)
C(10)–P–Ni	114.6(1)		

^a Cp is the cyclopentadienyl ring centroid.

Table 5
Selected bond lengths (Å) and bond angles (°) for **3a**

<i>Bond lengths</i>			
Ni–S	2.184(1)	Ni–P	2.145(1)
Ni–Cp ^a	1.752(3)	C(18)–S	1.761(3)
C(24)–N	1.271(3)	C(14)–P	1.820(2)
C(6)–P	1.822(2)	C(10)–P	1.834(2)
<i>Bond angles</i>			
S–Ni–Cp	131.6(1)	Cp–Ni–P	136.3 (1)
C(18)–S–Ni	109.7(1)	C(10)–P–Ni	113.7(1)
C(6)–P–Ni	113.4(1)	C(14)–P–Ni	115.2(1)
P–Ni–S	91.2(1)		

^a Cp is the cyclopentadienyl ring centroid.

Hz, OC_6H_4), 6.92 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.26 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.78 (q, 2H, OCH_2CH_2), 1.57–1.27 (m, 28H, alkoxy, butyl), 0.92 (m, 12H, butyl, alkoxy). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, δ ppm): 25.29. Anal. Found: C, 70.15; H, 9.04; N, 2.11. Calc. for $C_{40}H_{62}NOPSNi$: C, 69.16; H, 9.95; N, 2.02%.

2.8. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_{14}H_{29})$ (**7a**)

A green solid with a yield of 0.48 g (49%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.40 (s, 1H, $N=C(H)$), 7.81 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.62 (d, 2H, $J_{HH} = 8.4$ Hz, NC_6H_5), 6.95 (d, 2H, $J_{HH} = 8.4$ Hz, OC_6H_4), 6.94 (d, 2H, $J_{HH} = 8.4$ Hz, SC_6H_4), 5.27 (s, 5H, $\eta^5-C_5H_5$), 4.02 (t, 2H, OCH_2), 1.81 (q, 2H, OCH_2CH_2), 1.59–1.27 (m, 22H, alkoxy, butyl), 0.93 (t, 12H, alkoxy, butyl). Anal. Found: C, 70.87; H, 9.33; N, 1.62. Calc. for $C_{44}H_{70}NOPSNi$: C, 70.40; H, 9.40; N, 1.85%.

2.9. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_{16}H_{33})$ (**8a**)

Green crystals with a yield of 0.14 g (87%)b were isolated. 1H -NMR ($CDCl_3$, δ ppm): 8.39 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.6$ Hz, $C(H)C_6H_4$), 7.60 (d, 2H, $J_{HH} = 8.4$ Hz, NC_6H_4), 6.94 (d, 2H, $J_{HH} = 8.6$ Hz, OC_6H_4), 6.93 (d, 2H, $J_{HH} = 8.4$ Hz, SC_6H_4), 5.26 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.80–1.30 (m, 46H, alkoxy, butyl), 0.92 (t, 12H, alkoxy, butyl). $^{31}P\{^1H\}$ -NMR ($CDCl_3$, δ ppm): 22.31 (s). Anal. Found: C, 70.22; H, 10.52; N, 1.67. Calc. for $C_{46}H_{74}NOPSNi$: C, 69.96; H, 9.74; N, 1.73%.

2.10. $Ni(\eta^5-C_5H_5)(PBu_3)(SC_6H_4NC(H)C_6H_4OC_{20}H_{41})$ (**9a**)

A green solid with a yield of 0.21 g (19.5%) was isolated. 1H -NMR ($CDCl_3$, δ ppm): 8.40 (s, 1H, $N=C(H)$), 7.81 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.62 (d, 2H, $J_{HH} = 8.4$ Hz, NC_6H_4), 6.95 (d, 2H, $J_{HH} = 8.8$

Hz, OC₆H₄), 6.94 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, SC₆H₄), 5.27 (s, 5H, η^5 -C₅H₅), 4.01 (t, 2H, OCH₂), 1.81 (q, 2H, OCH₂CH₂), 1.52–1.27 (m, 34H, alkoxy, butyl), 0.93 (t, 3H, alkoxy, butyl). ³¹P{¹H}-NMR (δ ppm): 22.45. Anal. Found: C, 71.21; H, 10.26; N, 1.92. Calc. for C₅₀H₈₂NOPSNi: C, 71.93; H, 9.90; N, 1.68%.

2.11. Ni(η^5 -C₅H₅)(PPh₃)(SC₆H₄NC(H)C₆H₄C₆H₅) (1b**)**

A brown solid with a yield of 0.55 g (64%) was obtained. ¹H-NMR (CDCl₃, δ ppm): 8.36 (s, 1H, N=C(H)), 7.83 (d, 2H, $J_{\text{HH}} = 8.8$ Hz, C(H)C₆H₄), 7.68 (t, 6H, PPh₃), 7.49 (m, 15H, PPh₃, NC₆H₄, C₆H₅), 7.13 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, C(H)C₆H₄C₆H₅), 7.05 (d, 2H, $J_{\text{HH}} = 8.8$ Hz, SC₆H₄), 5.14 (s, 5H, η^5 -C₅H₅). Anal.

Found: C, 74.14; H, 5.42; N, 3.27. Calc. for C₄₂H₃₄NPSNi: C, 74.80; H, 5.08; N, 2.08%.

2.12. Ni(η^5 -C₅H₅)(PPh₃)(SC₆H₄NC(H)-C₆H₄OCH₂C₆H₅) (2b**)**

A green solid with a yield of 0.34 g (54%) was obtained. ¹H-NMR (CDCl₃, δ ppm): 8.51 (s, 1H, N=C(H)), 7.97 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, C(H)C₆H₄), 7.71 (m, 6H, PPh₃), 7.44 (m, 15H, PPh₃, OCH₂C₆H₅, NC₆H₄), 7.19 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, OC₆H₄), 6.90 (d, 2H, $J_{\text{HH}} = 8.4$ Hz, SC₆H₄), 5.30 (s, 2H, OCH₂), 5.15 (s, 5H, η^5 -C₅H₅). ³¹P{¹H}-NMR (δ ppm): 35.77. Anal. Found: C, 72.19; H, 5.20; N, 1.83. Calc. for C₄₃H₃₆NOPSNi: C, 72.79; H, 5.82; N, 1.97%.

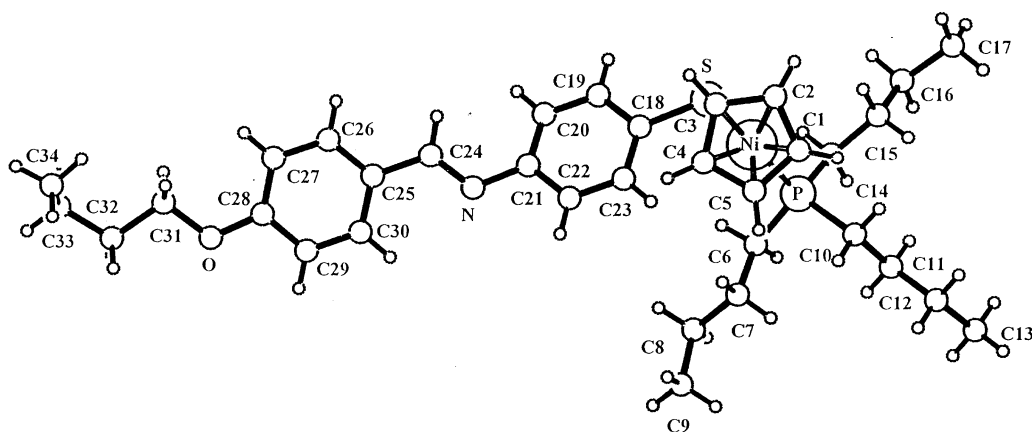


Fig. 5. Molecular structure of **3a**.

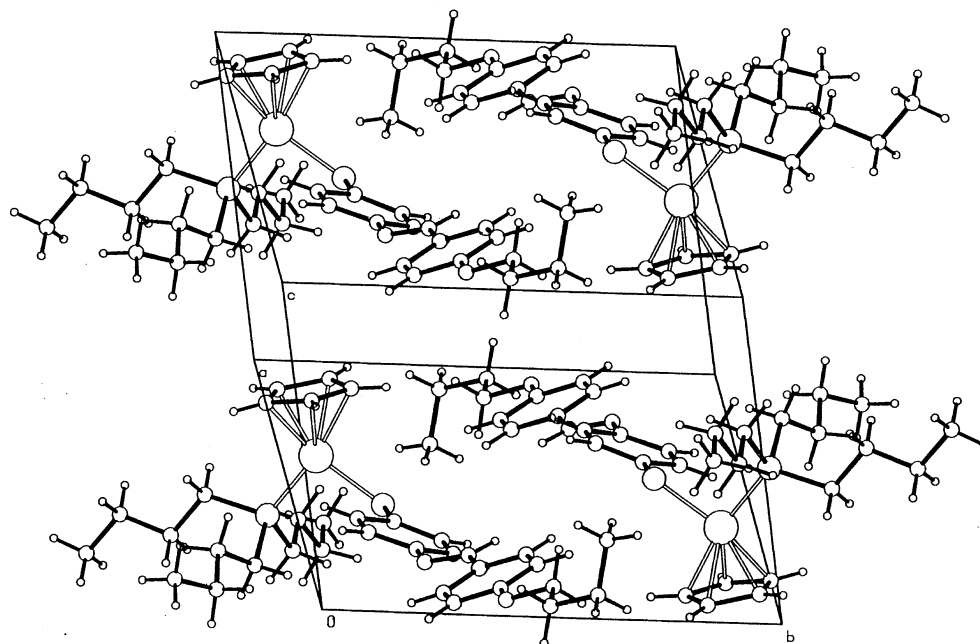


Fig. 6. Packing diagram for **3a**.

2.13. $Ni(\eta^5-C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4OC_4H_9)$
(**3b**)

A brown solid with a yield of 0.38 g (74%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.38 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.70 (t, 6H, PPh_3), 7.38 (s, 11H, PPh_3 , NC_6H_4), 6.95 (d, 2H, $J_{HH} = 8.4$ Hz, OC_6H_4), 6.85 (d, 2H, $J_{HH} = 6.4$ Hz, SC_6H_4), 5.13 (s, 5H, $\eta^5-C_5H_5$), 4.02 (t, 2H, OCH_2), 1.78 (q, 2H, OCH_2CH_2), 1.49 (q, 2H, $OCH_2CH_2CH_2$), 0.99 (t, 3H, CH_3). $^{31}P\{^1H\}$ -NMR (δ ppm): 35.40. Anal. Found: C, 71.89; H, 6.39; N, 2.11. Calc. for $C_{40}H_{38}NOPSNi$: C, 71.66; H, 5.71; N, 2.09%.

2.14. $Ni(\eta^5-C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4OC_8H_{17})$
(**5b**)

A brown solid with a yield of 0.33 g (87%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.38 (s, 1H, $N=C(H)$), 7.80 (d, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.71 (t, 8H, PPh_3 , NC_6H_4), 7.39 (m, 9H, PPh_3), 6.95 (d, 2H, $J_{HH} = 8.80$ Hz, OC_6H_4), 6.85 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.13 (s, 5H, $\eta^5-C_5H_5$), 4.02 (t, 2H, OCH_2), 1.78 (q, 2H, OCH_2CH_2), 1.6–1.16 (m, 10H, alkoxy), 0.88 (t, 3H, CH_3). ^{31}P -NMR ($CDCl_3$, δ ppm): 35.40. Anal. Found: C, 72.54; H, 6.44; N, 2.17. Calc. for $C_{44}H_{46}NOPSNi$: C, 72.41; H, 6.38; N, 1.93%.

2.15. $Ni(\eta^5-C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4OC_{10}H_{21})$
(**6b**)

A brown solid with a yield of 0.36 g (82%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.38 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.72 (t, 8H, PPh_3 , NC_6H_4), 7.39 (m, 9H, PPh_3), 6.95 (d, 2H, $J_{HH} = 8.8$ Hz, OC_6H_4), 6.85 (d, 2H, $J_{HH} = 8.8$ Hz, SC_6H_4), 5.13 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.78 (q, 2H, OCH_2CH_2), 1.58–1.28 (m, 14H, alkoxy), 0.89 (t, 3H, CH_3). ^{31}P -NMR ($CDCl_3$, δ ppm): 35.38. Anal. Found: C, 73.19; H, 6.79; N, 1.45. Calc. for $C_{46}H_{50}NOPSNi$: C, 73.22; H, 6.68; N, 1.86%.

2.16. $Ni(\eta^5-C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4OC_{14}H_{29})$
(**7b**)

A brick-red solid with a yield of 0.72 g (68.0%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.38 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4$), 7.70 (t, 6H, PPh_3), 7.38 (br s, 11H, PPh_3 , NC_6H_4), 6.95 (d, 2H, $J_{HH} = 8.8$ Hz, OC_6H_4), 6.85 (d, 2H, $J_{HH} = 8.4$ Hz

SC_6H_4), 5.13 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.80 (q, 2H, OCH_2CH_2), 1.26 (br s, 22H, alkoxy), 0.88 (t, 3H, CH_3). $^{31}P\{^1H\}$ -NMR (δ ppm): 35.41. Anal. Found: C, 73.82; H, 7.22; N, 1.32. Calc. for $C_{50}H_{58}NOPSNi$: C, 74.08; H, 7.21; N, 1.73%.

2.17. $Ni(\eta^5-C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4OC_{16}H_{33})$
(**8b**)

A brick-red solid with a yield of 0.49 g (77%) was obtained. 1H -NMR ($CDCl_3$, δ ppm): 8.38 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.4$ Hz, $C(H)C_6H_4$), 7.70 (m, 6H, PPh_3), 7.38 (m, 11H, PPh_3 , NC_6H_4), 6.95 (d, 2H, $J_{HH} = 8.40$ Hz, OC_6H_4), 6.85 (d, 2H, $J_{HH} = 8.6$ Hz, SC_6H_4), 5.13 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.80–1.25 (m, 28H, alkoxy), 0.88 (t, 3H, CH_3). Anal. Found: C, 74.22; H, 7.79; N, 1.53. Calc. for $C_{52}H_{62}NOPSNi$: C, 74.46; H, 7.45; N, 1.67%.

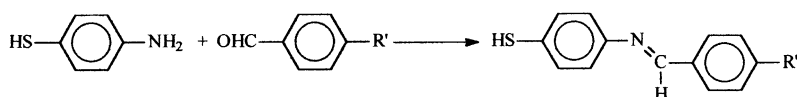
2.18. $Ni(\eta^5-C_5H_5)(PPh_3)(SC_6H_4NC(H)C_6H_4OC_{20}H_{41})$
(**9b**)

A brick-red solid with a yield of 0.75 g (65.0%) was isolated. 1H -NMR ($CDCl_3$, δ ppm): 8.31 (s, 1H, $N=C(H)$), 7.80 (d, 2H, $J_{HH} = 8.8$ Hz, $C(H)C_6H_4$), 7.70 (t, 6H, PPh_3), 7.38 (s, 11H, PPh_3 , NC_6H_4), 6.95 (d, 2H, $J_{HH} = 8.8$ Hz, OC_6H_4), 6.85 (d, 2H, $J_{HH} = 8.8$ Hz, SC_6H_4), 5.13 (s, 5H, $\eta^5-C_5H_5$), 4.01 (t, 2H, OCH_2), 1.78 (q, 2H, OCH_2CH_2), 1.27 (s, 34H, alkoxy), 0.88 (t, 3H, CH_3). $^{31}P\{^1H\}$ -NMR (δ ppm): 35.40. Anal. Found: C, 74.74; H, 7.15; N, 1.45. Calc. for $C_{56}H_{70}NOPSNi$: C, 75.08; H, 7.87; N, 1.56%.

3. Results and discussion

3.1. Synthesis of ligands

The Schiff base ligands, $HSC_6H_4NC(H)C_6H_4O-C_nH_{2n+1}$ ($n = 4$ (**3**), 6 (**4**), 8 (**5**), 10 (**6**), 14 (**7**), 16 (**8**), 20 (**9**)) and $HSC_6H_4NC(H)C_6H_4R''$ ($R'' = C_6H_5$ (**1**), $OCH_2-C_6H_5$ (**2**)), were prepared by condensation of equimolar amounts of 4-aminothiophenol and the appropriate aldehydes in ethanol Eq. (1). The products precipitated as yellow solids or thick oils within 30 min and were recrystallised from CH_2Cl_2 –hexane solution at $-15^\circ C$. The yields ranged from 60 to 100%. The analytical data of these ligands are presented in Table 1.



($R' = C_6H_4$, $OCH_2C_6H_5$, OC_nH_{2n+1} ; $n = 2, 4, 6, 8, 10, 14, 16, 20$)

3.2. Synthesis and characterisation of complexes

The above ligands were treated with either $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PBU}_3)\text{Br}$ or $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Br}$ to form the new complexes according to previously reported procedures [3]. The complexes were recrystallised from CH_2Cl_2 –hexane at -15°C to give analytically pure products in yields ranging from 30 to 88%. ^1H -NMR spectral data showed that thiolato resonance of the complexes and that of free ligands were very similar. Changes in the substituents of the thiolato ligands also had no significant influence on the electronic environment of either the cyclopentadienyl or the phosphine ligands. The ^1H -NMR spectra gave cyclopentadienyl resonance at 5.26–5.28 ppm (**1a–9a**) and 5.13–5.15 ppm (**1b–9b**) and ^{31}P -NMR spectra at ca. 22.4 ppm (**1a–9a**) and 35.5 ppm (**1b–9b**). These differences in peak values between the PBU_3 and PPh_3 complexes appear to be independent of the nature of the thiolato ligands. Similar chemical shifts have been reported for $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{X-4})$ ($\text{X} = \text{Cl}, \text{Br}, \text{NH}_2$) ($\text{R} = \text{Bu}$ (5.25, 22.4 ppm), $\text{R} = \text{Ph}$ (5.13, 35.4 ppm)) [17] and $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)(\text{SC}_6\text{H}_4\text{N=CHC}_6\text{H}_4\text{X-4'})$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{H}, \text{OH}, \text{Me}$; $\text{R} = \text{Bu}$ (5.27, 22.4 ppm), $\text{R} = \text{Ph}$ (5.14, 35.4 ppm)) [3]. The basicity of the phosphine thus determines the cyclopentadienyl resonance, with the more basic PBU_3 deshielding the cyclopentadienyl ligand.

3.3. Thermal studies

Thermal behaviour of the Schiff base ligands and their cyclopentadienylnickelphosphino complexes were investigated by TGA and DSC as well as polarising hot-stage microscope. They were generally stable up to 180°C before decomposing, however none of the ligands or the complexes showed any birefringence on heating and therefore are not liquid crystalline. The absence of liquid crystalline behaviour by the Schiff base compounds may be due to the terminal SH group. Most of organic compounds that are mesogenic feature nitro, cyano, halo, alkoxy or alkyl groups [18]. It is also known that when there is a potential for hydrogen bonding between molecules of a compound, mesogenic behaviour may be precluded [4a]. In the Schiff base ligands reported here the possibility of hydrogen bonding exists; which would involve the interaction of the thiol hydrogens with the alkoxy oxygens. Hydrogen bonding in the ligands is supported by the presence of $\text{S}\cdots\text{H}$ and $\text{N}\cdots\text{H}$ distances in the packing of **3a** (vide infra) that are in the range for hydrogen bonding [19]. Hence this could account for the lack of mesogenic properties when compounds **1–9** were heated.

The absence of mesogenic behaviour for the nickel complexes is also not surprising since there are no known bulky metal phosphine complexes that are liq-

uid crystals. In the known mesogenic metal phosphine complex $\text{Pt}(\text{PMe}_3)_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-OC}_n\text{H}_{2n+1})_2$ [20], the phosphine is less bulky. The lack of mesogenic behaviour for the PBU_3 and PPh_3 complexes might be due to their steric bulk, which prevents regular ordering on melting. This steric prevention to regular packing is also compounded by the presence of the cyclopentadienyl ring, which is out-of-plane of the phenyl rings of the thiolato ligand, as well as the geometry around the nickel centre. These are some of the issues that need to be addressed for these complexes to be mesogenic. One of the ways of concealing these features is to increase the number of rings in the ligand backbone [21].

Generally, the melting point of both the ligands and the complexes is dependent on the substituent in the 4' position of the ligand (Table 2). The PBU_3 complexes also melted at considerably lower temperatures than their PPh_3 analogues, some even 60°C lower. When the substituent was an alkoxy group, the longer the alkoxy chain length the lower the melting point; though some leveling off effect seem to set in when the alkoxy carbons exceeded 10. Similar levelling off of the melting points has previously been observed [22]. For phenyl and benzyloxy substituted ligands the melting points were higher than their alkoxy analogues.

From the TGA data two thermal decomposition pathways could be established which were dependent on the phosphine substituent. Complexes that have PPh_3 initially lost the cyclopentadienyl ligand followed by the loss of the phosphine and rapture of the Schiff base ligand (Scheme 1a). Fig. 1 shows representative TGA-DSC curves for the PPh_3 complex series, revealing three steps of the decomposition in the TGA and four peaks in the DTA. The first step in the decomposition sequence occurred at 180°C and corresponds to the loss of the cyclopentadienyl ligand accompanied by a large exothermic effect in the DSC curve. The second step is the gradual endothermic process in the temperature range $190\text{--}320^\circ\text{C}$ centred at 248.5°C , corresponding to the loss of PPh_3 ligand. In comparison to the PBU_3 complexes, the PPh_3 ligand is lost at a relatively higher temperature suggesting a stronger Ni–P bond. The third step centred at about 400°C was the exothermic rapture and subsequent loss of the Schiff base moiety, leaving a residual mass that corresponded to the $\text{Ni}(\text{SC}_6\text{H}_5)$ moiety. The PBU_3 analogue, on the other hand, decomposed first by simultaneous loss of cyclopentadienyl and phosphine ligand followed by the rupturing the Schiff base ligand (Scheme 1b). Fig. 2 shows representative TGA-DSC curves for PBU_3 complex series. The residual mass in all the cases correspond to a $\text{Ni}(\text{SC}_6\text{H}_5)$ moiety. The above thermal decomposition pathways demonstrate the relative strengths of the three Ni–ligand interactions. The strongest of these bonds appear to be the Ni–S bond in both types of complexes, which stays intact even at

temperatures above 800 °C. It is interesting to note that the Ni–P bonds of the more basic phosphine (PBU₃) only breaks around 200 °C, whilst those of the less basic phosphine (PPh₃) are only stable up to about 300 °C.

3.4. Molecular structures of **1a** and **3a**

The molecular structures of **1a** and **3a** determined by X-ray crystallography are shown in Figs. 3 and 5 and confirm that the proposed structures derived from the analytical data are correct. A selection of crystal data and structure refinement parameters for **1a** and **3a** is given in Table 3. Selected bond angles and distances for **1a** and **3a** are shown in Tables 4 and 5, respectively. The structures are typical of monocyclopentadienylnickel complexes that have a monophosphine ligand. The cyclopentadienyl centroid–nickel bond distances in **1a** and **3a** are 1.750(3) and 1.752(3) Å, respectively and lie within the range 1.743–1.764 Å found for complexes Ni(η^5 -C₅H₅)(PR₃)(SC₆H₄X) (R = Ph, Bu or Et; E = S, Se or Te; X = H, Cl or Me) and Ni(η^5 -C₅H₅)(PR₃)-(SC₆H₄NC(H)C₆H₄X-4) (R = Ph or Bu; X = Br or Me) [3,17,23]. The Ni–S distances in **1a** (2.184(1) Å) and **3a** (2.192(1) Å) and the Ni–P distances in **1a** (2.145(1) Å) and **3a** (2.145(1) Å) are all similar to distances of Ni–S bonds and Ni–P bonds in cyclopentadienylnickel(II) complexes. The N=C double bond is slightly longer at 1.271(3) Å, compared to 1.261(5) and 1.258(5) Å [24]. However, molecular packing in the unit cell of **1a** (Fig. 4) is different from the packing in Ni(η^5 -C₅H₅)(PPh₃)(SC₆H₄NC(H)C₆H₄Br-4) and Ni(η^5 -C₅H₅)(PBU₃)(SC₆H₄NC(H)C₆H₄Me-4) [3] the latter two having the same molecular packing as **3a** (Fig. 6). Even though packing in **1a** is also pairwise as in the two Schiff base nickel complexes above [3], the pairwise association in **1a** has a pair with cyclopentadienylnickel phosphine at one end. For the complexes Ni(η^5 -C₅H₅)(PPh₃)(SC₆H₄NC(H)C₆H₄Br-4) and Ni(η^5 -C₅H₅)(PBU₃)(SC₆H₄NC(H)C₆H₄Me-4) each pair consists of head-to-tail, tail-to-head packing, if the cyclopentadienyl end is considered to be the head. Thus the packing in **1a** is two head-to-tail molecular arrangements next to each other. The head-to-tail orientation in **1a** is partly due to the hydrogen bonds S1...H24 (3.101(2) Å) and N1...H36 (2.976(2) Å) that link two tails to each other. The distances are in the range found for hydrogen bonding [19]. Another feature in the structure of **1a** is that all three benzene rings of the thiolato ligand are not co-planar, with the ring next to the sulfur atom at right angles to the terminal ring.

4. Conclusions

Nickel complexes containing thiolato Schiff base ligands with long alkoxy chains are readily prepared.

Their thermal stability is independent of the nature of the phosphine but their decomposition pathways differ. Complexes containing PPh₃ have stronger Ni–P bonds compared to their PBU₃ analogues. Melting points of complexes were lower for all PBU₃ complexes compared to their PPh₃ analogues and were also progressively lower as the alkoxy chain length increased up to C₁₀ after which the melting point levelled off.

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