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Synthesis and characterisation of mono- and dinuclear diethyldithiocarbamatonickel(II) organochalcogenide complexes

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Abstract

The reaction of Ni(dtc)(PR_3)Cl (dtc=diethyldithiocarbamate, R=Ph or Bu) with HSC_6H_4Cl-4 or $HSCH_2C_6H_4Cl$-4 and Et_3N gave two types of complex. For PPh_3, the products were $[Ni(dtc)(\mu\text{-}SC_6H_4Cl\text{-}4)]_2$ (**1**) and $[Ni(dtc)(\mu\text{-}SCH_2C_6H_4Cl\text{-}4)]_2$ (**2**); whilst PBu_3 gave Ni(dtc)(PBu_3)(SC_6H_4Cl-4) (**3**). The structure of freshly prepared **3** was determined to be monomeric, as indicated by X-ray diffraction studies. However, at room temperature in solution, **3** was observed to slowly convert to **1**. Structural identification of **1** and **2** and similar dimers, and structural identification of **3** and analogous monomers, were investigated by mass spectrometry. Electron impact mass spectrometry (EIMS) failed to confirm the proposed structures due to extensive decomposition in the mass spectrometer. In the electron impact (EI) mode, all complexes invariably decomposed to $Ni(dtc)_2$; on the other hand, fast atom bombardment (FAB) ionisation gave the expected molecular ions for all compounds. © 1999 Elsevier Science Ireland Ltd. All rights reserved.

Keywords: Nickel thiolato complexes; Crystal structure; Mass spectrometry

1. Introduction

The nuclearity of nickel thiolato complexes appears to be highly dependent on the electron density at the nickel centre. The most common of these complexes are mono- and dinuclear compounds. Generally, complexes containing alkyl phosphine ancillary ligands form mononuclear compounds of the type $Ni(SR)_2L_2$ where R is an aryl group and L is aphosphine [1]. The presence of other ligands that influence the electron density on the central metal atoms have also been found to greatly affect the eventual structures of these thiolato complexes. For example, thiolato complexes formed from the reactions of Ni(dtc)(PPh_3)Cl, where dtc=diethyldithiocarbamate, and the appropriate thiol invariably leads to the formation of dinuclear compounds, which contain bridging thiolato ligands and the reactions are accompanied by loss of the phosphine [2]. However, replacing the sulfur with selenium results in either a monomeric or a dimeric complex, depending on the organic group attached to the chalcogen. For instance, aryl selenides form monomers whilst alkyl ones are dimers [3]. This has been attributed to the electronic effect the organic substituent has on the organochalcogenide ligands [3]. Those with electron-releasing ligands tend to form dinuclear compounds, as the increased electron density on the chalcogen allows the ligand to form a dative bond with a second nickel atom. Hence, to prepare monomeric compounds one needs to have the right balance between all three factors; namely, the phosphine, the chalcogen and the organic group attached to the chalocogen. In this paper, we report on the different types of complexes that are formed when the phosphine changes between PPh_3 and PBu_3, whilst the organic group is restricted to 4-chlorobenzyl, in an attempt to throw some light on the factors that influence monomer or dimer formation.

The second aspect of this report is on the use of mass spectrometry to determine the structural types of complexes described above. In our recent work [3], we attempted to establish the structures of these complexes by electron impact mass spectrometry (EIMS), without much success. The peaks found were mainly those of decomposition products. This seems to be closely linked to the ability of the compounds to withstand conditions in the ion source in order to produce molecular ions and has thus made EIMS a less attractive tool for establishing the structures of these compounds. Early literature reports seem to have circum-

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vented this by using alternative means to establish structures; for example, the dimeric structures of the chalcogen-bridged dithiobenzoatenickel(II), $[(C_6H_5CS_2)Ni(\mu\text{-}S)]_2$ and dithiocarbamatonickel(II), $[(C_6H_5NHCS_2)Ni(\mu\text{-}S)]_2^{2-}$ compounds were deduced from their molecular weight measurements [4]. However, molecular weight determinations are generally a less accurate structural technique. In instances where direct evidence was lacking, structural information had been deduced from that of the related compounds as in the thioxanthate compounds, $[(C_6H_5SCS_2)Ni(\mu\text{-}SCH_2C_6H_5)]_2$ [5] and $[(EtSCS_2)Ni(\mu\text{-}SEt)]_2$ [6], which are readily converted to the corresponding dithiocarbamate analogs by reacting them with triethylamine. Based on the X-ray structures of the thioxanthates [5,6], the dithiocarbamate complexes were inferred to be dimeric as well. When our attempts to establish the monomeric and dimeric structures of our compounds by EIMS were unsuccessful, we changed to softer ionization techniques like fast atom bombardment (FAB) and field desorption (FD) to show that both the monomeric and dimeric dithiocarbamate complexes that we have synthesised and those previously reported [2,3] can be routinely characterised, using the right ionization technique. These two ionization methods, which did not require high ion source temperatures, readily gave the molecular ions for all of the compounds investigated.

2. Experimental

2.1. Materials and instrumentation

All solvents were of analytical grade and were used without further purification. Tributylphosphine, triphenylphosphine, 4-chlorothiophenol, 4-chlorobenzylmercaptan and nitrobenzyl alcohol were purchased from Aldrich and used as received. The starting materials, $Ni(dtc)(PPh_3)Cl$ and $Ni(dtc)(PBu_3)Cl$, were prepared by the literature procedures [7]. All reactions were performed under a nitrogen atmosphere but the air-stable products were worked-up in air.

IR spectra were recorded on a Nicolet 205 FT-IR spectrometer. ^1H and ^{13}C NMR were recorded on a Varian Gemini 2000 spectrometer at 200 and 50.28 MHz, respectively, and referenced to residual $CHCl_3$ for ^1H (δ 7.26) and ^{13}C (δ 77.0). Elemental analyses were performed by the Microanalytical Laboratory at the University of Cape Town, South Africa, as a service.

2.2. Reaction of *Ni(dtc)(PPh$_3$)Cl* with 4-chlorothiophenol: formation of *[Ni(dtc)(μ-SC$_6$H$_4$Cl-4)]$_2$* **(1)**

A solution of $Ni(dtc)(PPh_3)Cl$ (0.70 g, 1.40 mmol) and $HSC_6H_4Cl\text{-}4$ (0.20 g, 1.40 mmol) in degassed toluene (50 mL) was reacted with Et_3N (0.20 mL). The solution immediately turned green and was stirred at room temperature for 2 h. The resultant mixture was filtered to remove Et_3NHCl and an equal volume of hexane was added. After cooling at −15°C overnight, green crystals of $[Ni(dtc)(\mu\text{-}SC_6H_4Cl\text{-}4)]_2$ were obtained. Yield=0.40 g, 81%. Anal. calc. for $C_{22}H_{28}Cl_2N_2S_6Ni_2$: C, 37.69; H, 4.06; N, 4.00. Found: C, 38.04; H, 4.49; N, 4.36. ^1H NMR ($CDCl_3$): δ 7.82 (d, 4H, $J_{HH}=8.55$ Hz, $SC_6H_4Cl\text{-}4$); 7.12 (d, 4H, $J_{HH}=8.55$ Hz, $SC_6H_4Cl\text{-}4$); 3.48 (q, 8H, dtc); 1.15 (t, 12H, dtc). $^{13}C\{^1H\}$ NMR: δ 136.4(s), 132.8(s), 131.3(s), 128.0(s) ($SC_6H_4Cl\text{-}4$); 43.8(s), 12.4(s) (dtc). IR (KBr pellet cm^{-1}): 2976 w, 2929 w, 2677 w, 1514 vs, 1472 m, 1439 s, 1387 m, 1277 s, 1209 m, 1151 s, 1086 s, 1010 s, 913 w, 815 s, 801 s, 739 w.

2.3. Reaction of *Ni(dtc)(PPh$_3$)Cl* with 4-chlorobenzylmercaptan: formation of *[Ni(dtc)(μ-SCH$_2$C$_6$H$_4$Cl-4)]$_2$* **(2)**

The reaction was performed and worked up in a manner similar to that in Section 2.2 using $Ni(dtc)(PPh_3)Cl$ (0.50 g, 1.00 mmol) and 4-chlorobenzylmercaptan (0.20 g, 1.07 mmol) to give $[Ni(dtc)(\mu\text{-}SCH_2C_6H_4Cl\text{-}4)]_2$ (**2**). Yield= 0.20 g, 55%. Anal. calc. for $C_{24}H_{32}Cl_2N_2S_6Ni_2$: C, 39.53; H, 4.44; N, 3.84. Found: C, 39.46; H, 4.73; N, 4.21. ^1H NMR ($CDCl_3$): δ 7.15 (d, 4H, $J_{HH}=8.36$ Hz, $SCH_2C_6H_4Cl\text{-}4$); 7.07 (d, 4H, $J_{HH}=8.36$ Hz, $SCH_2C_6H_4Cl\text{-}4$); 3.64 (q, 8H, dtc); 2.72 (s, 4H, $SCH_2C_6H_4Cl\text{-}4$); 1.26 (t, 12H, dtc). $^{13}C\{^1H\}$ NMR: δ 137.8(s), 132.2(s), 130.4(s), 128.3(s) ($SCH_2C_6H_4Cl\text{-}4$); 43.9(s) (dtc), 32.3(s), ($SCH_2C_6H_4Cl\text{-}4$); 12.5(s) (dtc). IR (KBr pellet cm^{-1}): 2972 w, 2927 w, 1521 vs, 1489 m, 1457 m, 1436 m, 1405 w, 1379 m, 1356 m, 1282 s, 1261 m, 1206 m, 1153 m, 1092 s, 1014 s, 910 w, 850 m, 804 s, 724 w, 668 w, 646 w, 504 m.

2.4. Reaction of *Ni(dtc)(PBu$_3$)Cl* with 4-chlorothiophenol: formation of *Ni(dtc)(PBu$_3$)(SC$_6$H$_4$Cl-4)*

To a solution of $Ni(dtc)(PBu_3)Cl$ (0.55 g, 1.00 mmol) and $HSC_6H_4Cl\text{-}4$ (0.15 g, 1.00 mmol) in toluene (30 mL) was added excess Et_3N (1 mL). The purple colour immediately changed to greenish–brown, accompanied by precipitation of a white solid. The mixture was stirred at room temperature for 4 h and filtered to remove the white solid of Et_3NHCl, which was washed with 2×5 mL of hexane. After the addition of hexane (20 mL), the filtrate was cooled at −15°C overnight to give green, X-ray quality crystals of $Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4)$. Yield=0.37 g, 71%. Anal. calc. for $C_{23}H_{41}ClNPS_3Ni$: C, 49.97; H, 7.46; N, 2.53. Found: C, 49.50; H, 7.35; N, 2.75. ^1H NMR ($CDCl_3$): δ 7.39 (d, 2H, $J_{HH}=8.40$ Hz, $SC_6H_4Cl\text{-}4$); 7.00 (d, 2H, $J_{HH}=8.40$ Hz, $SC_6H_4Cl\text{-}4$); 3.50 (q, 4H, dtc); 1.55 (m, 18H, PBu_3); 1.18 (t, 6H, dtc) 1.00 (t, 9H, PBu_3). IR (nujol mull cm^{-1}): 1515 vs, 1405 s, 1357 m, 1301 m, 1278 s, 1206 m, 1148 m, 1088 vs, 1072 s, 1009 s, 911 w, 850 w, 819 m, 799 w, 734 w, 724 w, 695 w, 545 w, 497 m, 468 w.

2.5. Crystal structure determination of $Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4)$

Single crystals for structural determination were grown by slow diffusion of hexane into a CH_2Cl_2 solution of **3**, which was cooled at −15°C. A green cube-like crystal was mounted in a sealed capillary tube on a Siemens SMART diffractometer, equipped with a CCD detector for geometric and intensity data collection. The structure was solved by the Patterson method for primary atom sites and by the difference map for atoms in secondary sites. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined without restraints. The structure was refined by full matrix least-squares on F^2 with a weighting scheme $w^{-1}=w^2(Fo^2)+(0.100P)^2+0.00P$, where $P=(Fo^2+2Fc^2)/3$, using SHELXL-93 [8]. An empirical absorption correction was applied to the data [9]. Crystal data and structure refinement details are listed in Table 1 and other pertinent information is deposited at the Cambridge Crystallographic Data Centre (deposition number 102412).

Table 1
Crystal data and structural refinement for **3**

Formula	$C_{23}H_{41}ClNPS_3Ni$
Fw	552.88
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P1 bar*
a (Å)	10.348(9)
b (Å)	10.761(9)
c (Å)	15.086(13)
α (deg)	102.93(10)
β (deg)	106.10(10)
γ (deg)	104.17(10)
Volume (Å^3), *Z*	1486.4(2), 2
density (calculated) (Mg m^{-3})	1.235
Abs coeff (mm^{-1})	1.018
F(000)	588
Crystal size (mm)	0.64×0.42×0.24
θ-range for data collected (deg)	1.48–25.53
Limiting indices	$-11\leq h\leq 12$ $-13\leq k\leq 10$ $-16\leq l\leq 18$
No. of reflections collected	5995
No. of independent reflections	448
R(int)	0.0622
Refinement method full-matrix least-squares on F^2	
Data/restraints/parameters	4446/0/276
Goodness of fit on F^2	0.893
Final *R* indices [$I>2\sigma(I)$]	$R_1=0.0977$ $wR_2=0.2650$
R indices (all data)	$R_1=0.1224$ $wR_2=0.2926$
Largest difference peak and hole (e Å^{-3})	1.212 and −0.748

2.6. Mass spectrometry

Mass spectrometry of all of the compounds was performed on a JMS-HX100 EBE spectrometer (JEOL, Japan). EI spectra were obtained at an electron energy of 70 eV, an emission current of 100 mA and an acceleration voltage of 5 kV. The ion source temperature was 250°C and the temperature of the EI direct insertion probe (DIP) was programmed from 50 to 250°C at 32°C/min. Fast atom bombardment (FAB) spectra of all of the compounds were obtained with nitrobenzyl alcohol (NBA) as the matrix. Argon fast atoms were used to bombard the samples, dissolved in the matrix, on a stainless steel probe tip. The ion source temperature was kept below 100°C to prevent decomposition of the compounds. The mass spectrometer was calibrated using CsI. Field ionization (FI) and field desorption (FD) spectra were obtained using the FAB+ acquisition parameters. The FD spectra were acquired at 50, 100 and 150°C. The optimum cathode voltage was 4.5 kV and the emitter current ramp program was 0–40 mA at 4 mA/min.

3. Results and discussion

3.1. Synthesis of complexes

The reaction of 4-chloro-substituted thiols with $Ni(dtc)(PR_3)Cl$ (R=Ph or Bu) gave two types of products, depending on the nature of the phosphine. When the phosphine was PPh_3, the reaction occurred as in Eq. (1) and was accompanied by the loss of PPh_3.

$$\mathrm{Ni(dtc)(PPh_3)Cl + HSR'} \xrightarrow[-\,\mathrm{PPh_3}]{\mathrm{Et_3N}} \tfrac{1}{2}[\mathrm{Ni(dtc)}(\mu\text{-}\mathrm{SR'})]_2 + \mathrm{Et_3NHCl}$$

$$[\mathrm{R'} = \mathrm{C_6H_4Cl\text{-}4}\ (\mathbf{1}),\ \mathrm{CH_2C_6H_4Cl\text{-}4}\ (\mathbf{2})] \qquad (1)$$

The ^{1}H NMR spectra of compounds **1** and **2** showed no PPh_3 peaks. The only phenyl protons were the two doublets assignable to the thiolato ligands. Confirmation of the absence of PPh_3 in the nickel complexes was obtained when PPh_3 was isolated from the filtrate after the nickel compounds had been filtered off. Our earlier work has shown that when R′ is a phenyl group, a similar dimeric compound, $[Ni(dtc)(\mu\text{-}SC_6H_5)]_2$ [2], is formed when the same reaction as that in Eq. (1) is performed with thiophenol (HSC_6H_5). However, the selenium analogue forms $Ni(dtc)(PPh_3)(SeC_6H_5)$ [3]. By replacing the hydrogen in the *para*-position with a halide, 4-chlorothiophenol formed $[Ni(dtc)(\mu\text{-}SC_6H_4Cl\text{-}4)]_2$, whilst the selenium analogue formed $Ni(dtc)(PPh_3)(SeC_6H_4Cl\text{-}4)$ [3]. The propensity towards dimer formation appears to be associated with two factors. First is the ability of the chalcogen to donate an electron pair to a second nickel atom. The second is the steric bulk of the phosphine. Thus, if the chalcogen has a strong donor ability like sulfur, the process of binding a second metal atom results in the loss of PPh_3. On the other hand, when aryl groups are attached to selenium, they form monomers, while their alkyl analogues give dimers. The former have less electron density on the selenium, while the latter are more electron-rich.

We tested this hypothesis by changing the phosphine in $Ni(dtc)(PR_3)Cl$ to PBu_3. On performing the reaction above with $Ni(dtc)(PBu_3)Cl$, we were able to isolate and characterise $Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4)$ (**3**) (Eq. (2)) by a combination of NMR spectroscopy and X-ray crystallography.

$$Ni(dtc)(PBu_3)Cl + HSC_6H_4Cl\text{-}4 \xrightarrow[-Et_3NHCl]{Et_3N} Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4) \quad (2)$$

Freshly prepared solutions of this product showed a ^1H NMR spectrum with two doublets in the phenyl region at 7.39 and 7.00 ppm. However, after one day, an additional set of doublets appeared at 7.81 and 7.12 ppm, which increased in intensity over a period of three days, suggesting that the monomeric compound decomposes in solution (Fig. 1). The new set of doublets is the same as those of **1** and indicates a gradual conversion of **3** to **1**, via a loss of PBu_3. Hence, even the less bulky PBu_3 seem to gradually give way to forming dimers in the presence of the electron-donating sulfur. Hence, it appears that the most important factor in maintaining the monomeric form is the ability of the chalcogen to donate electrons and that the steric factor might be secondary.

3.2. Structure of 3

The structure of **3** in the solid state was determined by X-ray crystallography. The molecular structure of **3** is shown in Fig. 2 and some of the relevant bond distances and angles are given in Table 2. The final *R* (0.0977) value is quite high, particularly when compared to the *R*(int) (0.0622). This might be due to some disorder and thus should account for the poor refinement. The high final *R*

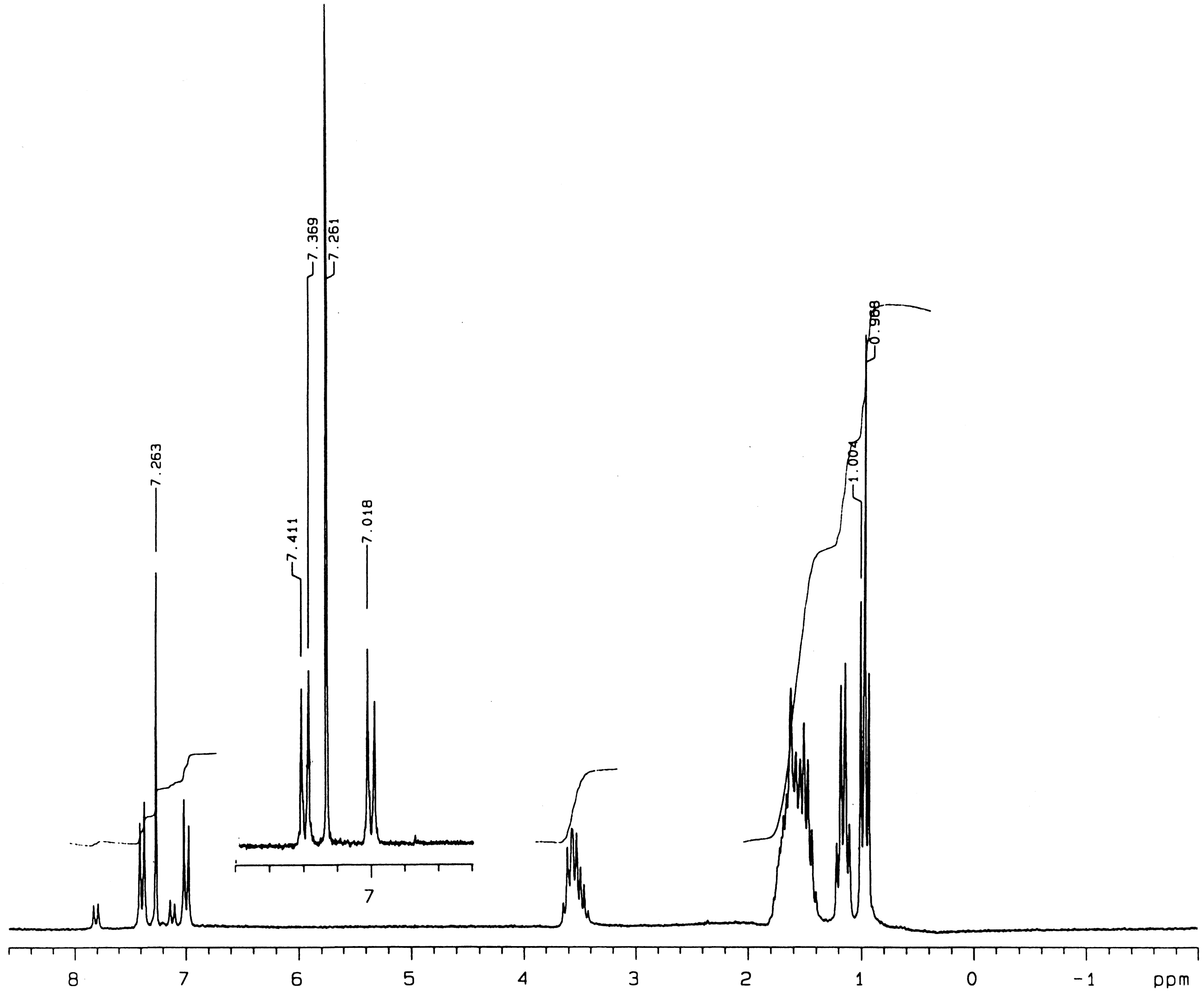


Fig. 1. ^1H NMR spectrum of $Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4)$ after 24 h and the spectrum of freshly prepared sample (insert).

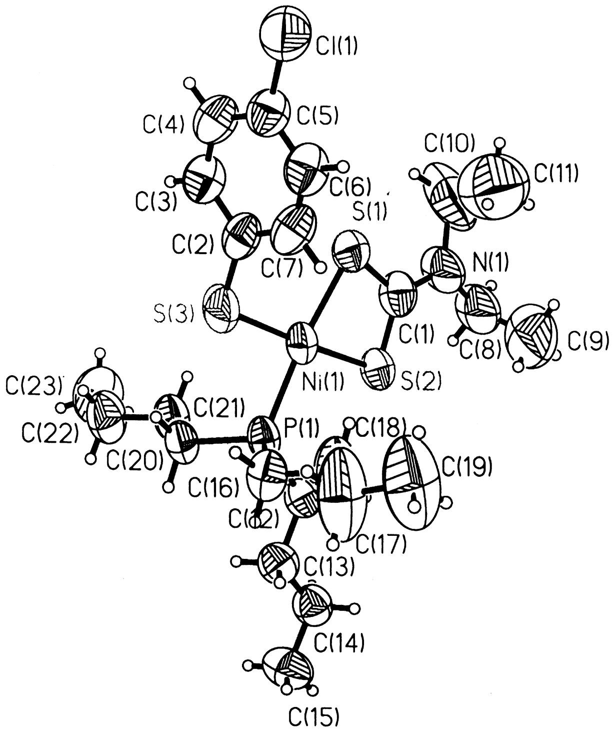


Fig. 2. Molecular structure of Ni(dtc)(PBu$_3$)(SC$_6$H$_4$Cl-4)

Table 2
Selected bond distances and angles for **3**

Bond distances (Å)			
Ni(1)–P(1)	2.169(2)	Ni(1)–S(1)	2.228(1)
Ni(1)–S(2)	2.210(2)	Ni(1)–S(3)	2.190(2)
P(1)–C(12)	1.842(6)	P(1)–C(16)	1.830(7)
P(1)–C(20)	1.832(6)	S(3)–C(2)	1.746(8)
S(1)–C(1)	1.733(7)	S(2)–C(1)	1.687(9)
C(1)–N(1)	1.330(10)	N(1)–C(8)	1.493(13)
N(1)–C(10)	1.630(2)	Cl(1)–C(5)	1.736(9)
Bond angles (°)			
P(1)–Ni(1)–S(1)	173.7(7)	P(1)–Ni(1)–S(2)	95.6(8)
P(1)–Ni(1)–S(3)	87.9(8)	S(2)–Ni(1)–S(3)	175.0(9)
S(1)–Ni(1)–S(3)	97.9(9)	S(1)–Ni(1)–S(2)	78.7(7)
Ni(1)–P(1)–C(12)	115.8(2)	Ni(1)–P(1)–C(16)	112.4(3)
Ni(1)–P(1)–C(20)	114.0(2)	C(1)–S(1)–Ni(1)	84.4(3)
C(1)–S(2)–Ni(1)	86.1(3)	Ni(1)–S(3)–C(2)	109.6(2)
N(1)–C(1)–S(1)	123.7(7)	N(1)–C(1)–S(2)	125.6(6)

value limits the extent to which the structural data can be discussed. Nevertheless, the crystal structure confirms what could be deduced from the analytical data. The geometry around the nickel is a distorted square plane. The distorted square planar environment of the nickel is similar to that of Ni(dtc)(PPh$_3$)(SeC$_6$H$_5$), if one considers the S(1), S(2), S(3) and the P atoms as occupying the corners of the square plane. The largest deviation from the square planar angle is the S(2)–Ni(1)–S(1) angle of 78.72(7)° and the least is the P(1)–Ni(1)–S(3) of 87.92°. The former appears to be the constraint the bidentate diethyldithiocarbamato ligand imposes on the nickel when bound to it. This angle was found to be the least in Ni(dtc)(PPh$_3$)(SeC$_6$H$_5$) [78.0(1)° [3] and largest in Ni(dtc)$_2$ (79.4(1)°] [10]. The Ni–S bond distances Ni(1)–S(1) [2.228(2) Å] and Ni(1)–S(2) [2.210(2) Å] of the Ni–dtc interaction in **3** are slightly longer than those in Ni(dtc)(PPh$_3$)(SeC$_6$H$_5$) [2.219(1) and 2.208(1) Å, respectively]. The Ni–S(3) bond to the thiolato ligand in **3** has a bond distance of 2.190(2) Å and is similar to that of (η^5-C$_5$H$_5$)Ni(PBu$_3$)(SC$_6$H$_4$Cl-4) (2.194(9) Å) [11]. The Ni–P distance [2.169(2) Å] though is slightly longer than that in (η^5-C$_5$H$_5$)Ni(PBu$_3$)(SC$_6$H$_4$Cl-4) [2.140(8) Å], it is within acceptable distances for Ni–P bonds for Ni in the +2 oxidation state, for example (η^5-C$_5$H$_5$)Ni(PPh$_3$)-(CH$_2$SO$_2$Ph) [2.150(1) Å] [12].

3.3. Mass spectra

In order to identify a mass spectrometric technique that could establish the structures of both the monomeric and dimeric complexes, we used electron impact (EI), fast atom bombardment (FAB) and field ionization/field desorption (FI/FD) ionization modes to study the following compounds: [Ni(dtc)(μ-SC$_6$H$_4$R′-4)]$_2$ (R′ = Cl (**1**), H (**4**), Me (**5**)), [Ni(dtc)(μ-SCH$_2$C$_6$H$_4$Cl-4)]$_2$ (**2**), [Ni(dtc)(μ-SeCH$_2$C$_6$H$_5$)]$_2$ (**6**), [Ni(dtc)(μ-SeMe)]$_2$ (**7**), [Ni(dtc)(μ-SeC$_6$H$_4$Cl-4)]$_2$ (**8**) (Table 3) and Ni(dtc)(PBu$_3$)(SC$_6$H$_4$Cl-4) (**3**), Ni(dtc)(PPh$_3$)(SeC$_6$H$_5$) (**9**) and Ni(dtc)(PPh$_3$)(SeC$_6$H$_4$Cl-4) (**10**) (Table 4). When the mass spectra of all of the compounds were investigated by EI ionization, none of them gave a molecular ion. Two prominent peaks, [Ni(dtc)$_2$]$^+$ (354) and those of the

Table 3
Correlation of *m/z* values for the important ions[a] in the FAB mass spectra of [Ni(dtc)(μ-ER)]$_2$ (E = S, Se)

Compound	Molecular ion	*a*	*b*	*c*	*d*	*e*	(CH$_3$)$_2$NCS
1	704	n.d.	557	n.d.	414	354	116
2	728	603	571	446	414	354	116
4	632	555	523	446	414	354	116
5	660	569	537	492	414	354	116
6	754	663	585	492	414	354	116
7	602	586	506	492	414	354	116
8	794	n.d.	605	492	414	354	116

[a] Refer to Scheme 1 for ion assignment, n.d. = not detected.

Table 4
FAB mass spectra of $Ni(dtc)(ER')(PR''_3)$

Compound	Molecular ion (*m/z*)	Other prominent fragments
3	551	$[Ni(dtc)(\mu\text{-}SC_6H_4Cl\text{-}4]_2^+$ (704), $[Ni_2(dtc)_2]^+$ (414)
9	625	$[Ni(dtc)(\mu\text{-}SeC_6H_5]_2^+$ (726) $[Ni_2(dtc)_2(SeC_6H_5)]^+$ (572), $[Ni_2(dtc)_2]^+$ (414), $Ni(dtc)_2]^+$ (354), $[PPh_3]^+$ (262)
10	659	$[Ni(dtc)(\mu\text{-}SeC_6H_4Cl\text{-}4]_2^+$ (796), $[Ni(dtc)(PPh_3)]^+$ (468), $[Ni_2(dtc)_2]^+$ (414), $[Ni(dtc)_2]^+$ (354), $[PPh_3]^+$ (262)

phosphines, $[PPh_3]^+$ (*m/z* 262) or $[PBu_3]^+$ (*m/z* 202), were found. Since all of the compounds investigated had previously been fully characterized by a combination of IR, NMR, elemental analyses and, in the case of $Ni(dtc)(PPh_3)(SeC_6H_5)$ [3] and $Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4)$, by X-ray crystallography (Fig. 2), the absence of molecular ions and the formation of $[Ni(dtc)_2]^+$ (*m/z* 354) by EIMS is an indication of thermal decomposition in the ion source of the mass spectrometer. However, it is difficult to deduce a structure for any of the complexes by putting together the fragments of the EI spectrum. This prompted us to use the softer ionization technique of FAB. Even here, the choice of matrix proved to be quite crucial to the successful acquisition of a meaningful mass spectrum showing the molecular ion. When glycerol was used as the matrix, only ions due to the matrix were observed. The most successful matrix was nitrobenzyl alcohol. Fig. 3 shows the FAB mass spectrum of $[Ni(dtc)(\mu\text{-}SC_6H_5)]_2$ and Table 3 lists all of the dimeric compounds examined. All of these compounds showed molecular ions in their respective spectra. That these compounds are all less stable relative to bis(diethyldithiocabarmato)nickel(II), $Ni(dtc)_2$, could clearly be established; in most instances, the ion due to $Ni(dtc)_2$ formed the base peak. This was particularly true for the EI spectra where all compounds produced $Ni(dtc)_2$ as the parent ion. The FAB mass spectral fragmentation pathway appears to be similar for all of the dimeric compounds and is proposed to occur in a sequential fashion, involving the loss of the organochalcogenide ligands, to produce the various ions in the spectra. The fragmentation pathways are depicted for $[Ni(dtc)(\mu\text{-}SCH_2C_6H_4Cl\text{-}4]_2$ in Scheme 1, which shows the stepwise loss of $SCH_2C_6H_4Cl\text{-}4$ and Ni, to give $Ni(dtc)_2$. In contrast to the EI spectra, the fragments from the FAB spectra could be seen as sequential loss of units from the molecular ions, thus, confirming the structure suggested by the molecular peaks.

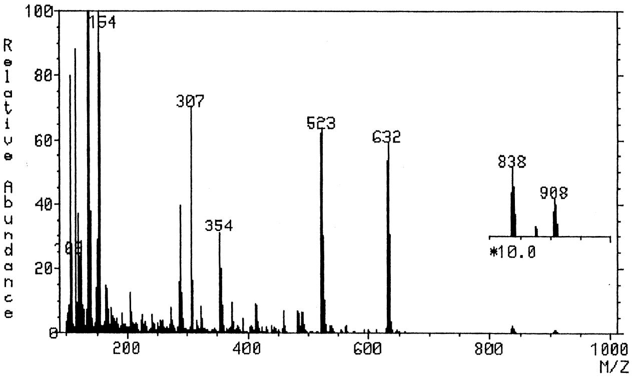
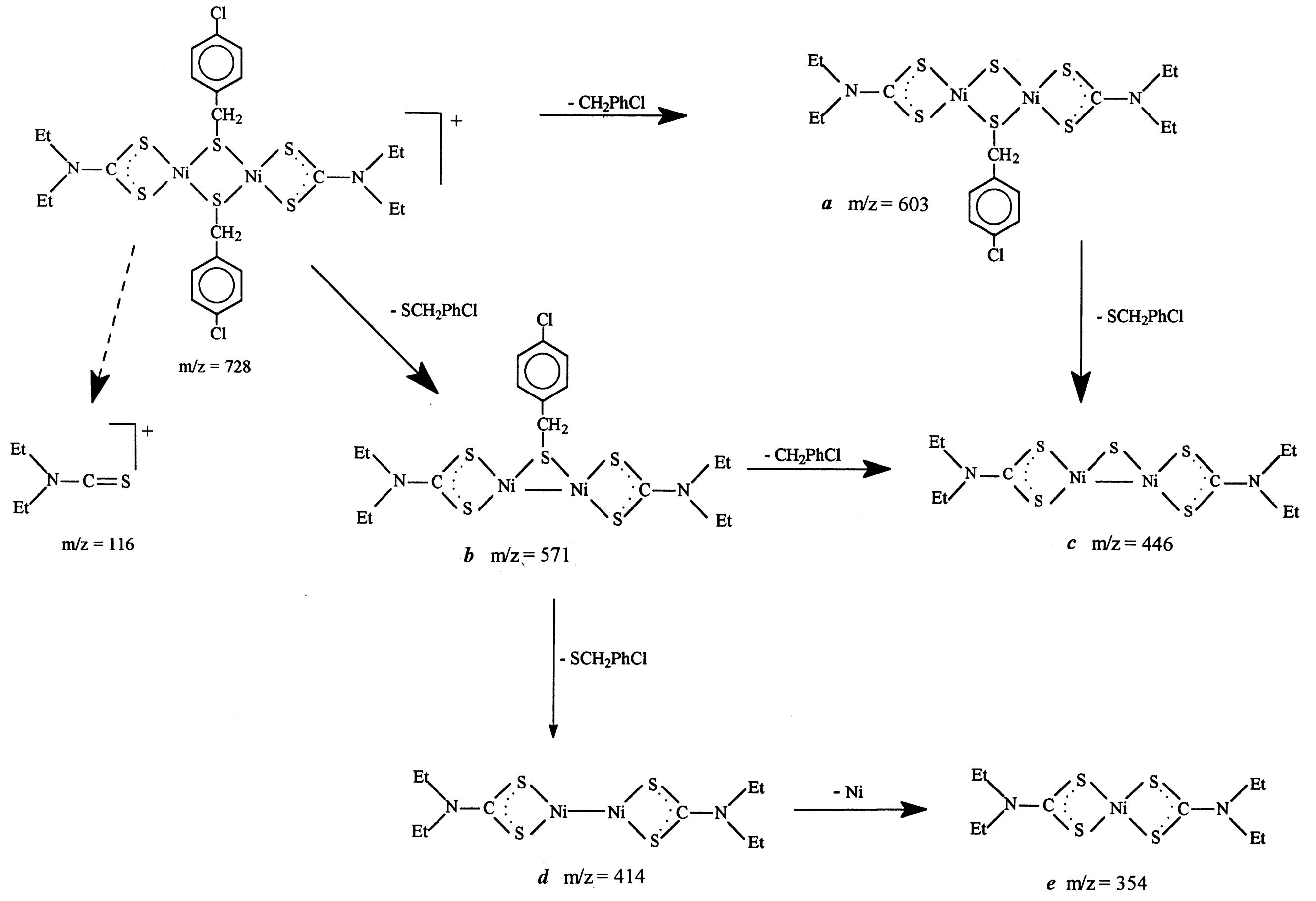


Fig. 3. FAB spectrum of $[Ni(dtc)(\mu\text{-}SC_6H_5)]_2$.

It was not clear whether the EI spectrum was the result of thermal decomposition in the ion source or due to electron impact fragmentation. However, we suspected that thermal decomposition could be the major process responsible for the spectra we were observing. To test this hypothesis, both FI and FD of three compounds (**1**, **2** and **3)** were studied. In the FIMS analysis, the compounds needed to be heated to evaporate them into the ion source, while the FDMS did not require heating to enable their ionization. It was observed that the FI spectra of these compounds were different from those of the EI and FD spectra. Unlike the FDMS, the compounds appeared to decompose with heating, thus giving $Ni(dtc)_2$ as a cluster of ions at *m/z* 354 in both FIMS and EIMS. However, unlike the EIMS, the FIMS seemed to have different ionization pathways. Ions that were prominent in the EI spectra were observed to be minor in the FI spectra and vice versa. A cluster of ions were observed at *m/z* 710 in all of the FI spectra and these were interpreted to be coming from the dimerization of $Ni(dtc)_2$, which leads to the formation of $[Ni(dtc)(\mu\text{-}dtc)]_2$.

When the same crystalline samples from which crystals were selected for the X-ray structural determination of $Ni(dtc)(PPh_3)(SeC_6H_5)$ and $Ni(dtc)(PBu_3)(SC_6H_4Cl\text{-}4)$ were subjected to FABMS analysis, molecular ions corresponding to the solid state structures were found (Table 4). In addition, ions corresponding to the dimers $[Ni(dtc)(\mu\text{-}SeC_6H_5)]_2^+$ (*m/z* 726) and $[Ni(dtc)(\mu\text{-}SC_6H_4Cl\text{-}4)]_2^+$ (*m/z* 704) were observed. A typical spectrum showing both the molecular ions of the monomer and the decomposed dimer of $Ni(dtc)(PPh_3)(SeC_6H_5)$ is shown in Fig. 4. Even though, in solution, the ^1H NMR of



Scheme 1.

Ni(dtc)(PBu$_3$)(SC$_6$H$_4$Cl-4) shows a monomer/dimer equilibrium with time, the time frame required for the monomer/dimer equilibrium is much longer than that needed to obtain the mass spectrum. The dimer formation here is also believed to take place in the mass spectrometer but via a process that is completely different from that observed in solution by NMR. A similar observation was made from the spectrum of a microcrystalline sample of Ni(dtc)(PPh$_3$)(SeC$_6$H$_4$Cl-4), which has a monomeric peak of *m/z* 659 and a dimeric peak of *m/z* 796 for [Ni(dtc)(μ-SeC$_6$H$_4$Cl-4)]$_2^+$. There are two viable decomposition pathways for the monomers, all of which have identifiable fragments in the spectra. The first is the simultaneous loss of the phosphino and the organochalcogenide ligands to form Ni(dtc)$_2$. The second route involves the loss of only the phosphino ligand, which generates the electron-deficient species Ni(dtc)(ER) and its subsequent dimerization to [Ni(dtc)(μ-ER)]$_2$ (E = S, Se) (Scheme 2). Further decomposition of the dimers follows the same pathway as in Scheme 1. The strength of the dithiocarbamate as a ligand in the decomposition is quite clear. It forms most of the identifiable species in the spectra. The stability of dithiocarbamate as a ligand for Pt(II) in mass spectral studies has been noted by Colton and Tedesco [13,14]. This allows the formation of stable ions in the gaseous phase, which helps in identifying complexes.

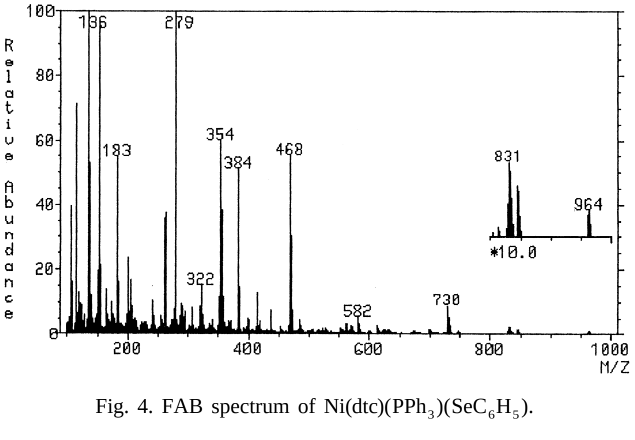


Fig. 4. FAB spectrum of Ni(dtc)(PPh$_3$)(SeC$_6$H$_5$).

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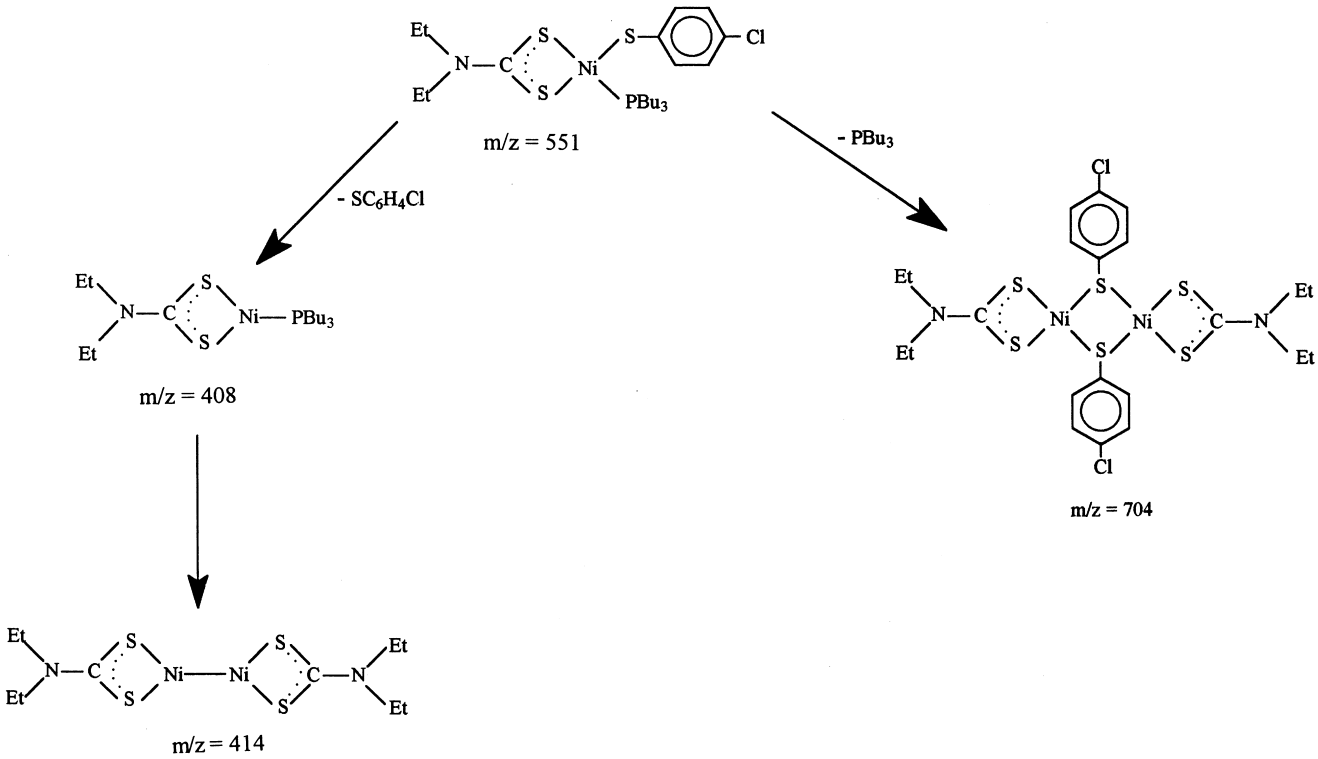

Scheme 2.

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