DALTON
FULL PAPER

Anion dependent deprotection of a thioether group in Schiff base NS_2 ligands results in new mononuclear and dinuclear thiolato nickel complexes

Elisabeth Bouwman,*[a] Richard K. Henderson,[a] Annie K. Powell,[b] Jan Reedijk,[a] Wilberth J. J. Smeets,[c] Anthony L. Spek,[c] Nora Veldman[c] and Sigrid Wocadlo[b]

[a] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: bouwman@chem.leidenuniv.nl*
[b] *School of Chemical Sciences, University of East Anglia, Norwich, UK NR4 7TJ*
[c] *Bijvoet Centre for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

Received 13th July 1998, Accepted 1st September 1998

The synthesis and characterisation of three Schiff base compounds of nickel with NS_2 donor groups is described as part of our research in structural modelling of nickel hydrogenase enzymes. 2-Aminothiophenol and 2-*tert*-butylthiobenzaldehyde reacted in ethanol to form a benzothiazolidine derivative, which is isolated as a yellow solid. The benzothiazolidine ring opens upon reaction with nickel acetate in ethanol to form a mononuclear complex, $[Ni(^tBuL^1)_2]$, **1**, which crystallises in the monoclinic space group $P2_1/n$ with cell dimensions, $a = 14.665(4)$, $b = 14.800(7)$, $c = 14.923(6)$ Å, $\beta = 94.45(3)°$. Compound **1** is mononuclear with a *cis* N_2S_2 chromophore, which is square planar, but slightly distorted towards tetrahedral, and which shows weak interactions with two hydrogens of the ligands (Ni–H distances of 2.52 and 2.58 Å). These C–H · · · Ni interactions are retained in solution as reflected in the ^{1}H NMR spectra of **1**. With other nickel salts, the same benzothiazolidine ligand reacts in ethanol to form dinuclear species $[Ni(L^1)]_2$ **2**, after loss of the protecting tertiary butyl group. Complex **2** crystallises in the monoclinic space group $P2_1/c$ with cell dimensions, $a = 11.753(3)$, $b = 11.977(3)$, $c = 20.275(4)$ Å, $\beta = 123.67(1)°$. An analogous ligand, synthesised from 2-aminoethanethiol and 2-*tert*-butylthiobenzaldehyde, was not isolated, but was used in a template reaction with nickel salts in ethanol to form the dinuclear compound $[Ni(L^2)]_2$ **3**. Complex **3** crystallises in the monoclinic space group $P2_1/c$ with cell dimensions $a = 15.049(4)$, $b = 10.554(2)$, $c = 12.921(4)$ Å, $\beta = 108.68(2)°$. Compounds **2** and **3** are dinuclear, in a 'butterfly' shape, with bridging thiolates. The nickel ions in these two dinuclear complexes are in a NS_3 chromophore with a square planar geometry.

Hydrogenase enzymes, which are found in natural micro-organisms, are used in the (reversible) oxidation of dihydrogen.[1] The metal-containing hydrogenase enzymes are usually grouped into one of two general classifications, *i.e.* Fe-only, or [NiFe] hydrogenases, of which the latter has a subclass of selenocysteine containing [NiFeSe] hydrogenases.[2] Subsequently, even a hydrogenase lacking any metal ions has been reported.[3] The [NiFe] hydrogenases consist of enzymes which, apart from iron, also contain nickel in the active site. The first crystal structure of a [NiFe] hydrogenase enzyme, extracted from *Desulfovibrio gigas*, in which the unusual nature of the active site was revealed, has been published by Volbeda *et al.* in 1995.[4] The active site was shown to contain an unexpected disulfur-bridged heterobimetallic Ni–Fe core. There are two further cysteine groups bound to the nickel and three small non-protein ligands bound to the iron. These diatomic ligands are nowadays considered to be one carbon monoxide and two cyanide molecules, based on isotopic enrichment experiments and FTIR measurements.[5] The publication of the crystal structure has renewed interest in the chemical modelling of the active site of [NiFe] hydrogenases. A large amount of modelling chemistry had already been reported prior to the publication of the crystal structure,[6] when it was believed that the active site contained mononuclear nickel.

The three compounds described in this paper were synthesised as part of research in modelling the heterodinuclear Ni–Fe active site of hydrogenases. It was decided that ligands containing mixed N/S donor groups would be used preferentially to provide greater synthetic control. Previous work resulted in mononuclear compounds with square planar *cis* NiN_2S_2 chromophores.[7] However, reaction of these complexes with suitable iron complexes did not result in the desired Ni–Fe heterodinuclear compounds, and several new ligands were designed and synthesised. This has resulted in an interesting dinuclear iron compound as a good structural model for Fe-only hydrogenases.[8]

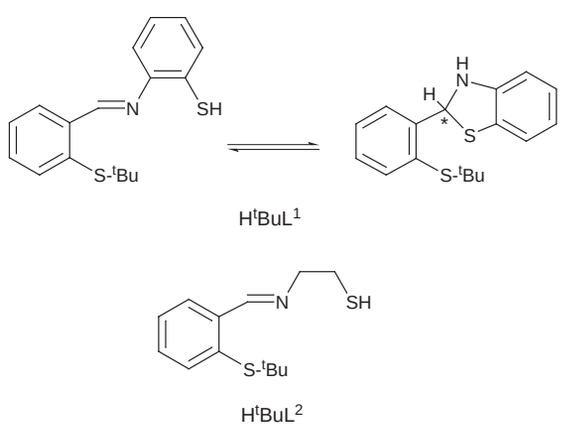

Fig. 1 Schematic drawing of the target ligands H^tBuL^1 and H^tBuL^2.

A schematic drawing of the target ligands described in this paper is given in Fig. 1. Loss of the protecting *tert*-butyl group upon complexation with nickel salts should lead to tridentate ligands with one imino nitrogen and two thiolato sulfur donors.

The use of the potentially tridentate benzothiazolidine ligand in complexation with nickel salts results in a mononuclear and a dinuclear nickel compound, depending on the anion used.

Experimental

General remarks

All synthetic procedures were performed in a nitrogen or argon atmosphere using solvents that were degassed on a vacuum system prior to use. 2-*tert*-Butylthiobenzaldehyde was prepared according to a literature procedure.[9] Microanalysis measurements were performed at the Microanalytical Laboratory of the University College, Dublin. Infrared spectra (KBr pellets) were recorded in the range 4000–400 cm^{-1} using a Perkin-Elmer FTIR Paragon spectrophotometer controlled by a PC using PE Grams Analyst software. Nuclear magnetic resonance spectra were recorded on a Bruker dpx300 MHz spectrometer.

Syntheses

2-(2-*tert*-Butylthiophenyl)benzothiazolidine (H^tBuL^1). To a solution of 2-*tert*-butylthiobenzaldehyde (1.1 g, 5.67 mmol) in 20 cm^3 toluene was added a solution of 2-aminothiophenol (94–96%, 0.61 cm^3, 5.67 mmol) in 20 cm^3 toluene. The mixture was heated under reflux for 2 h in the presence of $CaSO_4$ as a drying agent. The resultant bright yellow solution was dried over Na_2SO_4, filtered and the solvent evaporated, leaving a yellow oil. Recrystallisation in hexane–diethyl ether resulted in a yellow solid (58% yield) (Calc. for $C_{17}H_{19}NS_2$: C, 67.73; H, 6.35; N, 4.65; S, 21.27. Found: C, 67.58; H, 6.31; N, 4.64; S, 21.62%). IR (cm^{-1}) 3371s, 3063m, 2953m, 2857m, 1577s, 1469vs, 1456s, 1434m, 1398m, 1361s, 1321m, 1300m, 1266m, 1249m, 1189w, 1163s, 1117s, 1060w, 1039m, 783w, 751vs, 743vs, 711w, 693w, 668w, 636w, 589w, 515w, 423w. ^1H NMR ($CDCl_3$), δ 7.97 (1H, dd, J = 1.5, 7.8), 7.55 (1H, dd, J = 1.4, 7.6), 7.39 (1H, dt, J = 1.4, 7.4), 7.27 (1H, dt, J = 1.7, 7.5), 7.18 (1H, s, H*), 7.03 (1H, dd, J = 1.2, 7.5), 6.94 (1H, dt, J = 1.4 and 6.3), 6.75 (1H, dt, J = 1.3, 7.5), 6.67 (1H, dd, J = 1.0 and 7.8 Hz), 4.35 (1H, br s, NH), 1.32 (9H, s, Bu^t). ^{13}C NMR ($CDCl_3$), δ 147.0 (sm), 146.4 (sm), 139.8 (sm), 138.5, 131.1 (sm), 129.7, 128.0, 127.6, 125.9 (sm), 125.3, 123.1 (sm), 121.6, 120.5, 109.7, 66.9 (C*), 47.5, 31.1, 30.7 (sm). The peaks marked sm are small peaks that grow with time, and are peaks arising from the slow adjustment of the equilibrium of 2-(2-*tert*-butylthiophenyl)benzothiazolidine with *N*-(2′-*tert*-butylbenzylidene)-2-aminothiophenol, the open chain form of H^tBuL^1.

[Ni($^tBuL^1$)$_2$] 1. To a solution of the benzothiazolidine H^tBuL^1 (0.64 g, 2.10 mmol) in 20 cm^3 of absolute ethanol was added a solution of nickel acetate (0.26 g, 1.05 mmol) in 20 cm^3 of absolute ethanol. The mixture was heated under reflux conditions for 1 h during which time it turned dark red. On cooling, a dark red precipitate formed and was collected by filtration. X-Ray quality crystals were grown from chloroform–propan-2-ol. Yield 65% (Calc. for $C_{34}H_{36}N_2NiS_4$: C, 61.91; H, 5.50; N, 4.25; S, 19.44. Found: C, 61.94; H, 5.59; N, 4.31; S, 19.16%). IR (cm^{-1}) 3048w, 2957s, 2857m, 1593s, 1580m, 1573s, 1463m, 1455s, 1435m, 1364s, 1273m, 1256m, 1218w, 1179m, 1162s, 1123m, 1063s, 1027m, 952w, 894w, 755vs, 736s, 728s, 705m, 687m, 571m, 554w, 493w, 455w, 437w. UV–VIS in $CHCl_3$, λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 450 (4.3×10^3). ^1H NMR ($CDCl_3$), δ 10.95 (2H, d, J = 8), 8.38 (2H, s, HC=N), 7.56 (2H, d, J = 8), 7.40 (2H, d, J = 8), 7.34 (2H, t, J = 8), 7.01 (2H, t, J = 8), 6.95 (2H, t, J = 8), 6.69 (2H, t, J = 8), 6.27 (2H, d, J = 8 Hz), 1.21 (18H, s).

[Ni(L^1)]$_2$ 2. A mixture of 2-*tert*-butylthiobenzaldehyde (1.0 g, 5.15 mmol), 2-aminothiophenol (94–96%, 0.55 cm^3, 5.15 mmol) and nickel tetrafluoroborate (1.75 g, 5.15 mmol) was dissolved in 50 cm^3 of absolute ethanol. The mixture was heated under reflux conditions for 2 h. After a few minutes a grey-green precipitate formed, but this dissolved after 15 min and the solution became very dark red. On cooling, the very dark red precipitate that was formed was collected by filtration. Recrystallisation in toluene produced crystals that were suitable for single crystal X-ray diffraction. Yield 68% (Calc. for $C_{26}H_{18}N_2Ni_2S_4$: C, 51.69; H, 3.00; N, 4.64; S, 21.23. Found: C, 52.0; H, 2.72; N, 5.23; S, 20.81%). IR (cm^{-1}) 3054w, 1582s, 1562s, 1517s, 1452s, 1415m, 1391m, 1266m, 1248m, 1225m, 1177m, 1160w, 1129m, 1077s, 1026m, 952m, 751vs, 719s, 574m. UV–VIS in $CHCl_3$, λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 408 (1.5×10^4), 550 (4.4×10^3). ^1H NMR ($CDCl_3$), δ 8.65 (2H, d, J = 10), 8.61 (2H, s, HC=N), 7.80 (2H, d, J = 10), 7.72 (dd, 2H, J = 2, 8), 7.52 (2H, dd, J = 2, 8), 7.42 (2H, dt, J = 2, 8), 7.32 (2H, dt, J = 2, 8), 7.22 (2H, dd, J = 2, 8), 7.13 (2H, dt, J = 2, 8 Hz).

[Ni(L^2)]$_2$ 3. 2-Aminoethanethiol hydrochloride (0.78 g, 6.9 mmol, 10% excess with respect to sodium) was added to a solution of sodium (0.14 g, 6.2 mmol) in 30 cm^3 of absolute ethanol and the reaction mixture was stirred for 20 min. The white precipitate of solid NaCl was removed by filtration and the filtrate was added to a solution of 2-*tert*-butylthiobenzaldehyde (1.21 g, 6.2 mmol) in 20 cm^3 of absolute ethanol. This mixture was heated gently for 15 min before solid nickel acetate (1.55 g, 6.2 mmol) was added and the resulting solution was heated under reflux for 1 h. The solution turned dark red. On cooling a solid precipitated, which was collected by filtration. The crude product was dissolved in a mixture of 30 cm^3 chloroform and 20 cm^3 demineralised water. The two layers were separated and the aqueous layer was extracted three times with chloroform. The combined chloroform layers were dried over Na_2SO_4, and precipitation of the pure product was induced by addition of ethanol. Red crystals of [Ni(L^2)]$_2$ were grown from chloroform–propan-2-ol. Yield 36% (Calc. for $C_{18}H_{18}N_2Ni_2S_4$: C, 42.56; H, 3.57; N, 5.51; S, 25.25. Found: C, 42.37; H, 3.48; N, 5.60; S, 25.8). IR (cm^{-1}) 2960w, 1600s, 1587s, 1532s, 1459s, 1417m, 1406m, 1326m, 1269w, 1250w, 1219s, 1161w, 1128m, 1081s, 1051w, 1030m, 985w, 951w, 929w, 869w, 753vs, 719s, 695w, 636w, 452w, 378m. UV–VIS in $CHCl_3$, λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 380 (1.2×10^4), 490 (3.6×10^3). ^1H NMR ($CDCl_3$), δ 7.97 (2H, s, HC=N), 7.75 (2H, d, J = 8), 7.29 (2H, dd, J = 1, 8), 7.22 (2H, dt, J = 1, 8), 7.00 (2H, dt, J = 1, 8), 4.07 (2H, ddd, J = 2, 5, 12), 3.96 (2H, ddt, J = 2, 5, 12), 2.60 (2H, dt, J = 5, 12), 2.10 (2H, ddd, J = 2, 5, 12 Hz).

Crystallography

The crystal data and the refinement parameters for **1**, **2** and **3** are collected in Table 1.

[Ni($^tBuL^1$)$_2$] 1. The structure was solved using direct methods and subsequent Fourier-difference techniques, and refined anisotropically by full-matrix least squares on F^2 (SHELX-TL[10]). The H atoms were located by difference syntheses and refined isotropically using a riding model.

[Ni(L^1)]$_2$ 2. Reflection profiles were broad and structured. Correction for absorption was found to be unnecessary. The structure was solved with automated Patterson techniques[11] using DIRDIF 92 and refined on F^2 using SHELXL 96.[12] Hydrogen atoms were introduced on calculated positions and refined riding on the atoms they are attached to. The structure contains small voids of 29 $Å^3$, however no residual density was found in those areas as indicated by PLATON/SQUEEZE.[13]

[Ni(L^2)]$_2$ 3. Data were collected for absorption with PLATON/DELABS.[13] The structure was solved by Patterson techniques (DIRDIF 92)[11] and refined on F^2 with SHELXL 93.[14] Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms.

Table 1 Crystal and refinement data for the structures [Ni(^{t}BuL^1)$_2$] **1**, [Ni(L^1)]$_2$ **2** and [Ni(L^2)]$_2$ **3**

Complex	**1**	**2**	**3**
Formula	$C_{34}H_{36}N_2NiS_4$	$C_{26}H_{18}N_2Ni_2S_4$	$C_{18}H_{18}N_2Ni_2S_4$
M_r	659.60	604.08	508.00
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	14.665(4)	11.753(3)	15.049(4)
b/Å	14.800(7)	11.977(3)	10.554(2)
c/Å	14.923(6)	20.275(4)	12.921(4)
β/°	94.45(3)	123.67(1)	108.68(2)
V/Å^3	3229(2)	2375.3(9)	1944.1(9)
μ(Mo-Kα)/mm^{-1}	0.866	1.96	2.37
T/K	193(2)	150	150
Reflections collected	3429	7550	6385
No. unique reflections	3228	3738	4495
Observed [$I > 2\sigma(I)$]	3224	1686	2538
R_{int}	0.0660	0.1027	0.0650
R [$I > 2\sigma(I)$]	0.0520	0.0657	0.0682
wR [$I > 2\sigma(I)$]	0.1506	0.1205	0.1339

* Details in common: crystal system, monoclinic; $Z = 4$.

CCDC reference number 186/1146.

See http://www.rsc.org/suppdata/dt/1998/3495/ for crystallographic files in .cif format.

Results and discussion

Syntheses

The ligands and their nickel coordination compounds were synthesised using Schiff base chemistry. Spectroscopic measurements on the yellow powder isolated from the reaction of 2-*tert*-butylthiobenzaldehyde with 2-aminothiophenol indicate that the actual structure is not the expected open chain imine, but has a benzothiazolidine structure as depicted in Fig. 1. This is deduced from a strong N–H stretch in the infrared spectrum at 3371 cm^{-1}, and the absence of an imino signal in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum of the benzothiazolidine contains a peak at δ 66.9 which can be assigned to the chiral carbon atom. Similar reactions forming benzothiazolidines from substituted 2-mercaptoanilines have been reported before.[15] In solution an equilibrium exists of the benzothiazolidine ring structure with *N*-(2-*tert*-butylbenzylidene)-2-aminothiophenol, the open chain form of H^{t}BuL^1.

On reaction with nickel salts, the action of the ligand coordinating to nickel *via* N opens the benzothiazolidine ring regenerating the imine group. The N–H stretch in the infrared spectrum disappears and a signal arising from an imino C–H appears in the proton NMR spectrum of the formed nickel coordination compounds. Only when using nickel acetate in the complexation reaction, complex **1**, [Ni(^{t}BuL^1)$_2$], was synthesised from a reaction of the isolated ligand. The fact that complex **1** is a mononuclear nickel complex demonstrates an effect of using nickel acetate in the synthesis. The acetate group is a weak base in the alcoholic solvent. This helps stabilise the thioether group in the ligand leaving the *tert*-butyl group in place. When other nickel salts are used in syntheses with this ligand, another compound, [Ni(L^1)$_2$] **2**, is formed from the reaction of the benzothiazolidine ligand. The other counter ions that have been used in this reaction are chloride, tetrafluoroborate and perchlorate. As all of these resulted in the formation of **2**, BF_4^- was the anion of choice for the reactions, as with this anion it appeared to be relatively easy to check for (anion-containing) impurities in the IR spectra. However, the synthesis of **2** from the isolated benzothiazolidine results in very low yields of product and small impurities of **1**; a template (one-pot) synthesis produced much higher yields, and crystals suitable for X-ray diffraction could be obtained after recrystallisation of the crude product from toluene. Complex **1** is also a stable intermediate in the formation of the dinuclear nickel compound **2**: refluxing a solution of **1** in toluene ultimately leads to the formation of pure **2**.

No attempts have been undertaken to isolate the target ligand H^{t}BuL^2, expected to be formed from the reaction of 2-*tert*-butylthiobenzaldehyde and 2-aminoethanethiol. The metal salt was added to a gently warmed mixture of the two organic starting materials, and thus, in a template reaction compound **3**, [Ni(L^2)$_2$] was formed and isolated in reasonable yield.

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Ni1–N1	1.918(7)	Ni1–H9	2.575(9)
Ni1–N2	1.925(8)	Ni1–C9	3.083(9)
Ni1–S2	2.168(3)	Ni1–H26	2.517(9)
Ni1–S1	2.171(3)	Ni1–C26	3.09(1)
N1–Ni1–N2	96.6(3)	H9–Ni1–H26	146.8(3)
N1–Ni1–S2	166.8(2)	H9–Ni1–S1	113.1(2)
N2–Ni1–S2	87.3(2)	H9–Ni1–S2	97.2(2)
N1–Ni1–S1	86.8(2)	H9–Ni1–N1	71.2(3)
N2–Ni1–S1	167.3(2)	H9–Ni1–N2	79.5(3)
S2–Ni1–S1	92.12(13)	H26–Ni1–S1	95.4(3)
		H26–Ni1–S2	98.4(3)
C9–H9–Ni1	134.0(3)	H26–Ni1–N1	94.8(3)
C26–H26–Ni1	109.0(3)	H26–Ni1–N2	72.2(3)

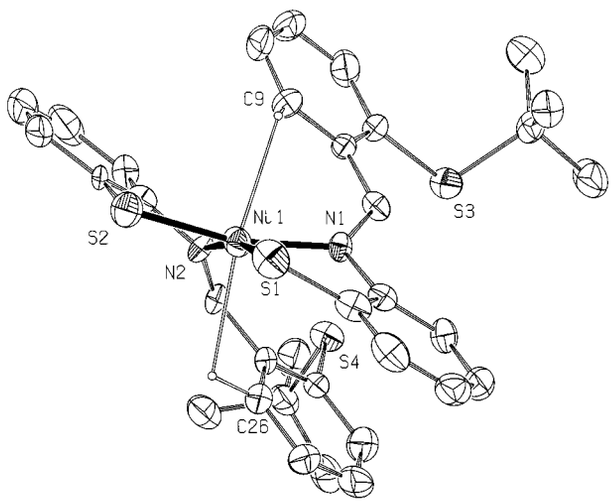

Fig. 2 A PLUTON projection of [Ni(^{t}BuL^1)$_2$] **1** with the atomic labelling of selected atoms. The nickel-to-hydrogen interactions are shown, the other hydrogen atoms are omitted for clarity.

Description of the structures

[Ni(^{t}BuL^1)$_2$] 1. A projection of the structure of **1** is shown in Fig. 2, and a selection of bond lengths and angles is given in Table 2. The nickel is in a distorted square planar *cis*-N_2S_2 coordination environment. The coordinating donor atoms are arranged around the nickel ion in a square plane with a slight tetrahedral twist; the atoms N1 and S2 are lying 0.2 Å above, and the atoms N2 and S1 lying 0.2 Å below the least squares plane calculated through the nickel ion and the four donor atoms. The plane Ni1N1S1 makes a dihedral angle of 18.6(3)° with the plane Ni1N2S2. The Ni–N and Ni–S distances of about 1.92 and 2.17 Å, respectively, are slightly longer than those observed in the more regular square planar compounds **2** and **3** (see below), possibly due to the slight deviation from planarity in the coordination geometry. The coordinating nitrogen and sulfur donor groups are both derived from 2-aminothiophenol, which results in the formation of two five-membered chelating rings around the nickel ion. This is one contributing factor to the slight distortion of nickel from square-planar geometry, because of the limited bite angle of

Table 3 Selected bond lengths (Å) and angles (°) for **2**

Ni1···Ni2	2.697(2)		
Ni1–S1	2.135(3)	Ni2–S2	2.194(4)
Ni1–S2	2.184(3)	Ni2–S3	2.139(4)
Ni1–S4	2.211(4)	Ni2–S4	2.194(3)
Ni1–N18	1.890(12)	Ni2–N32	1.906(14)
S1–Ni1–S2	172.82(16)	S2–Ni2–S3	93.56(15)
S1–Ni1–S4	94.05(15)	S2–Ni–S4	79.04(14)
S1–Ni1–N18	98.4(3)	S2–Ni2–N32	166.7(4)
S2–Ni1–S4	78.89(14)	S3–Ni2–S4	172.59(17)
S2–Ni1–N18	88.7(3)	S3–Ni2–N32	98.7(4)
S4–Ni1–N18	166.9(3)	S4–Ni2–N32	88.7(4)

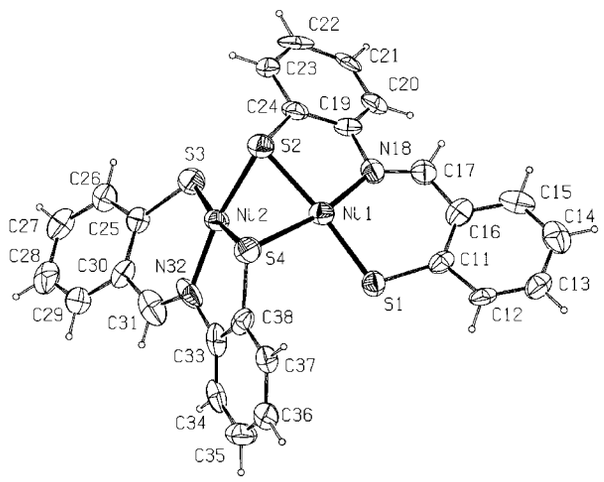

Fig. 3 A PLUTON projection of $[Ni(L^1)]_2$ **2** with the atomic labelling.

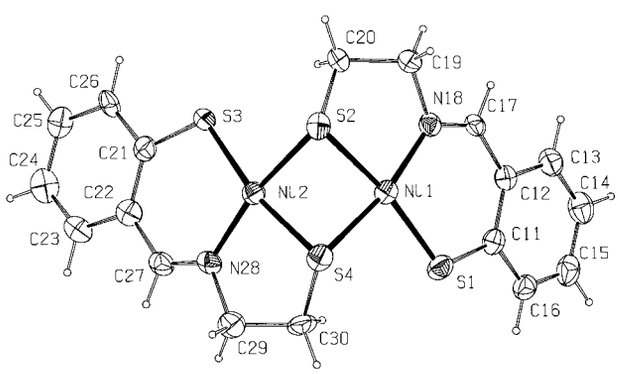

Fig. 4 A PLUTON projection of $[Ni(L^2)]_2$ **3** with the atomic labelling.

approximately 87°. The major origin of the tetrahedral twist is probably due to the *cis* coordination of the ligands, giving rise to steric hindrance of the remaining bulky groups. The *cis* coordination of the two ligands, and the folding of the ligands around nickel is apparently stabilised by stacking of the phenyl rings. Intramolecular stacking is observed between the *tert*-butylthiophenyl group of the one ligand onto the phenylene backbone of the other and *vice versa*, resulting in stacking distances of 3.19 and 3.32 Å. Intermolecular stacking is observed for the dangling phenylene groups with distances of 3.17 and 3.35 Å.

The two dangling phenylene groups also show an interaction with the nickel ion. In fact, a moderate interaction between the nickel ion and H9 and H26 is observed, with distances of only 2.58 and 2.52 Å respectively (see Table 2). Considering these interactions as bonding, the coordination geometry of the nickel ion could be described as pseudo-octahedral, in an $H_2N_2S_2$ chromophore, in which two hydrogen atoms occupy the axial sites of the octahedron. The projection of the structure given in Fig. 2 shows this semi-bonding interaction.

Table 4 Selected bond lengths (Å) and angles (°) for **3**

Ni1···Ni2	2.8141(16)		
Ni1–S1	2.133(2)	Ni2–S2	2.200(2)
Ni1–S2	2.198(2)	Ni2–S3	2.135(3)
Ni1–S4	2.192(2)	Ni2–S4	2.198(2)
Ni1–N18	1.881(6)	Ni2–N28	1.886(6)
S1–Ni1–S2	170.71(10)	S2–Ni2–S3	91.75(9)
S1–Ni1–S4	91.70(9)	S2–Ni2–S4	79.14(9)
S1–Ni1–N18	98.57(18)	S2–Ni2–N28	168.8(2)
S2–Ni1–S4	79.31(8)	S3–Ni2–S4	169.15(10)
S2–Ni1–N18	90.22(17)	S3–Ni2–N28	99.1(2)
S4–Ni1–N18	168.92(18)	S4–Ni2–N28	89.7(2)

$[Ni(L^1)]_2$ 2 and $[Ni(L^2)]_2$ 3. Projections of the structures of **2** and **3** are shown in Figs. 3 and 4, and a selection of the bond lengths and angles are given in Tables 3 and 4, respectively. Both compounds are dinuclear, with each nickel centre coordinated by one tridentate NS_2 ligand, one arm of which forms a sulfur bridge to the second nickel centre. The *tert*-butyl protecting groups on the thioether sulfurs of the ligands have been removed during the synthesis of the complexes, and the newly formed thiolate sulfurs are now coordinated to nickel. In both structures the initially unprotected thiolate sulfurs are the bridging ones, the deprotected thiolate groups are coordinating terminally. The nickel ions in both structures are in a slightly distorted square planar environment. For both structures the bond distances and angles around the nickel ion are comparable. The Ni–N distances are about 1.89 Å and the Ni–S bond lengths are in the range of 2.13 (terminal) to 2.21 Å (bridging). Nevertheless, the Ni···Ni distances are significantly different, being 2.697(2) Å for **2** and 2.814(2) Å for **3**. The overall shape of the dinuclear nickel complexes can be described as a 'butterfly', with the wings formed by the planes of the donor atoms around each nickel. The angle between the wings of the butterflies (least squares planes calculated through the four donor atoms) is 103.2(2)° for **2** and 107.9(1)° for **3**. The longer Ni···Ni distance in **3** can be explained by the presence of the aliphatic instead of the phenylene backbone, the puckering of which allows flattening of the butterfly, which is also reflected in the dihedral angles described above. The torsion angles in the five membered chelate rings are in the range of 10 to 20° in the phenylene backbone, and are about 40° in the ethylene backbone. No significant stacking of the aromatic rings is observed in these structures.

Discussion. The most reactive sulfurs in the mononuclear complex **1**, clearly are the two thioether sulfurs. Attempts to react **1** with either an iron complex, with methyl iodide, or just heating **1** in toluene all result in the formation of the dinuclear compound $[Ni(L^1)]_2$ **2**, after the displacement of one of the ligands and the removal of the *tert*-butyl group of the thioether group. Although the crystal structure of **1** shows a tetrahedral twist in the coordination plane of the nickel ion, the distortion from square planar is not severe enough to affect the magnetic properties of this complex, which is diamagnetic and therefore NMR active. A large shift of some of the protons is observed, notably for the protons which are involved in an interaction with the nickel ion. The resonances for these protons are found at δ 10.95 in $CDCl_3$ solution, which indicates that the weak C–H···Ni interaction is maintained in solution. The downfield shift of these protons in the NMR spectrum, and the fact that they are pointing in the direction of the occupied d_{z^2}-orbital of the nickel(II) ion indicate that these interactions are better described as hydrogen bonding rather than agostic interactions.[16]

The tetrahedral distortion in compound **1** is larger than some found in complexes in which a biphenyl backbone is used.[17] Frydendahl *et al.* have studied the properties of nickel thiolato Schiff base NiN_2S_2 compounds containing a biphenyl back-

bone, studying the influence of the tetrahedral twist on the geometry and the spin state of the nickel ion.[17] One of the mononuclear nickel complexes in that study is formed from 2-mercaptobenzaldehyde and 2,2′-diamino-6,6′-dimethylbiphenyl, and is similar to complex **1**, apart from the larger chelate ring and the 'connection' between the dangling phenylene rings. The tetrahedral twist in that compound is smaller than in **1**, as shown by the smaller dihedral angle of 14.4° compared to our 18.6°. This smaller tetrahedral twist is probably due to the more flexible six-membered chelate ring.

Dinuclear nickel complexes with structures similar to compounds **2** and **3** have been reported with monodentate,[18,19] or didentate ligands,[20] or a mixture of these two.[21] Furthermore, several similar structures with tridentate ligands have been reported.[19,22] In the case of mononuclear bridging thiolates the two nickel coordination planes can be coplanar (folding angle 180°), resulting in Ni···Ni distances up to 3.35 Å. Care must be taken when comparing the folding angles, as some authors calculate the folding angle using the planes formed by nickel and the two bridging thiolates, whereas others use the planes defined by the four donor atoms in the coordination plane of the nickel ions, which may result in a flattening of the 'butterfly'. An overview of Ni···Ni distances and folding angles in such compounds has been reported,[19] and an attempt to correlate the Ni···Ni distance with the folding angle has been undertaken.[21] The smallest Ni···Ni distance of 2.64 Å has been reported by Colpas *et al.*,[19] who claim that the folding angle in their compound (105.2°) is the most acute for this type of compound. However, the folding angle in compound **2** (103.2°) is smaller, but the Ni···Ni distance (2.70 Å) is somewhat longer than the one reported by Colpas *et al.*

The reaction of dinuclear compounds, such as **2** and **3**, with monodentate ligands may lead to splitting of the thiolate bridges, resulting in mononuclear complexes. Several reactions with thiolates, cyanide or pyridine type mononuclear ligands have been reported.[23] Attempts to perform this type of reactions with **2** or **3** are underway.

Conclusion

The three complexes presented in this work were all synthesised with the aim of creating a suitable nickel synthon that would show reactivity towards iron complexes, allowing one to create a good structural model for the active Ni–Fe site of the hydrogenase enzyme found in *D. gigas*. Although the model complex **1** contained the required feature of two *cis* sulfur atoms coordinated to a nickel, they were not found to be reactive towards iron complexes, and therefore further studies were not performed. Some interesting features are demonstrated by these complexes, such as the relative stability against polymerisation of the Ni–S bonds of thiophenol derivatives (as in ligand L^1), allowing the trapping of a mononuclear nickel complex **1**. The increased reactivity of Ni–S bonds of aliphatic thiols leads immediately to the formation of Ni–S–Ni bridges, as shown in complex **3**, thus not allowing any mononuclear nickel complex to be isolated whatever the nickel salt used. Despite the potential of the aromatic thiolates in **1** to form bridges to another metal, as is shown in **2**, attempts to react compound **1** with suitable iron complexes unfortunately thus far did not result in the formation of heterodinuclear NiFe complexes, but in the dinuclear compound **2** instead.

Acknowledgements

Financial support for this project has been provided by a BIOTECH grant (Contract no. BIO2-CT94-2041) from the European Union. The research of E. B. has been made possible by a Fellowship of the Royal Netherlands Academy of Arts and Sciences. The work was in part (W. J. J. S., A. L. S., N. V.) supported by The Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organisation for Scientific Research (NWO). The support of the Wellcome Trust is gratefully acknowledged (U. E. A.).

References

1 M. W. W. Adams, L. E. Mortenson and J. S. Chen, *Biochim. Biophys. Acta*, 1980, **594**, 105.
2 E. G. Graf and R. K. Thauer, *FEBS Lett.*, 1981, **136**, 165; M. W. W. Adams and L. E. Mortenson, *J. Biol. Chem.*, 1984, **259**, 7045; E. C. Hatchikian, N. Fourget, V. M. Fernandez, R. Williams and R. Cammack, *Eur. J. Biochem.*, 1992, **209**, 357.
3 R. K. Thauer, A. R. Klein and G. C. Hartmann, *Chem. Rev.*, 1996, **96**, 3031.
4 A. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *Nature* (*London*), 1995, **373**, 580; A. Volbeda, E. Garcin, C. Piras, A. L. deLacey, V. M. Fernandez, E. C. Hatchikian, M. Frey and J. C. Fontecilla-Camps, *J. Am. Chem. Soc.*, 1996, **118**, 12989.
5 R. P. Happe, W. Roseboom, A. J. Pierik, S. P. J. Albracht and K. A. Bagley, *Nature* (*London*), 1997, **385**, 126.
6 J. C. Fontecilla-Camps, *J. Bioinorg. Chem.*, 1996, **1**, 91; M. A. Halcrow and G. Christou, *Chem. Rev.*, 1994, **94**, 2421.
7 R. K. Henderson, E. Bouwman, J. Reedijk and A. K. Powell, *Acta Crystallogr.*, *Sect. C*, 1996, **52**, 2696; W. J. J. Smeets, A. L. Spek, R. K. Henderson, E. Bouwman and J. Reedijk, *Acta Crystallogr.*, *Sect. C*, 1997, **53**, 1564.
8 V. E. Kaasjager, R. K. Henderson, E. Bouwman, M. Lutz, A. L. Spek and J. Reedijk, *Angew. Chem.*, *Int. Ed.*, 1998, **37**, 1668.
9 O. Meth-Cohn and B. Tarnowski, *Synthesis*, 1978, 58.
10 G. M. Sheldrick, SHELXTL (version 5.03) Siemens Analytical X-ray Instruments Inc., Madison, WI, 1993.
11 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. García-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF 92 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.
12 G. M. Sheldrick, SHELXS 96, Program for crystal structure solution, University of Göttingen, 1996.
13 A. L. Spek, *Acta Crystallogr.*, *Sect. A*, 1990, **34**, C34.
14 G. M. Sheldrick, SHELXL93, Program for crystal structure refinement, University of Göttingen, 1993.
15 L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.*, 1968, **7**, 1149; L. F. Lindoy, D. H. Busch and V. Goedken, *J. Chem. Soc.*, *Chem. Commun.*, 1972, 683; T. Kawamoto, H. Huma and Y. Kushi, *Chem. Commun.*, 1996, 2121; A. Müller, K. U. Johannes, W. Plass, H. Bögge, E. Krahn and K. Schneider, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1765.
16 W. Yao, O. Eisenstein and R. H. Crabtree, *Inorg. Chim. Acta*, 1997, **254**, 105.
17 H. Frydendahl, H. Toftlund, J. Becher, J. C. Dutton, K. S. Murray, L. F. Taylor, O. P. Anderson and E. R. T. Tiekink, *Inorg. Chem.*, 1995, **34**, 4467.
18 A. D. Watson, C. P. Rao, J. R. Dorfman and R. H. Holm, *Inorg. Chem.*, 1985, **24**, 2820.
19 G. J. Colpas, M. Kumar, R. O. Day and M. J. Maroney, *Inorg. Chem.*, 1990, **29**, 4779.
20 B. S. Snyder, C. P. Rao and R. H. Holm, *Aust. J. Chem.*, 1986, **39**, 936; J. R. Nicholson, G. Christou, J. C. Huffman and K. Folting, *Polyhedron*, 1987, **6**, 863.
21 S. B. Choudhury and A. Chakravorty, *Inorg. Chem.*, 1992, **31**, 1055.
22 D. J. Baker, D. C. Goodall and D. S. Moss, *Chem. Commun.*, 1969, 325; G. A. Barclay, E. M. McPartlin and N. C. Stephenson, *Acta Crystallogr.*, *Sect. B*, 1969, **25**, 1262; S. B. Choudhury, M. A. Pressler, S. A. Mirza, R. O. Day and M. J. Maroney, *Inorg. Chem.*, 1994, **33**, 4831.
23 H.-J. Krüger and R. H. Holm, *Inorg. Chem.*, 1989, **28**, 1148; S. A. Mirza, M. A. Pressler, M. Kumar, R. O. Day and M. J. Maroney, *Inorg. Chem.*, 1993, **32**, 977; R. Hahn, A. Nakamura, K. Tanaka and Y. Nakayama, *Inorg. Chem.*, 1995, **34**, 6562.

Paper 8/05428B