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New nickel complexes with an S_4 coordination sphere; synthesis, characterization and reactivity towards nickel and iron compounds

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Abstract

Three new nickel complexes have been synthesized with the ligands Hbss (4-mercapto-2-thia-1-butylbenzene) and Hbsms (2-(benzylsulfanyl)-2-methyl-1-propanethiol). [Ni(bss)$_2$] is a mononuclear complex with an S_4 coordination environment. [Ni$_3$(bss)$_4$](BF$_4$)$_2$ and [Ni$_3$(bsms)$_4$](BF$_4$)$_2$ are linear trinuclear complexes that can be synthesized either directly from the ligands Hbss and Hbsms in a reaction with Ni(BF$_4$)$_2$, or via the mononuclear complexes [Ni(bss)$_2$] and [Ni(bsms)$_2$] in a reaction with Ni(BF$_4$)$_2$. These reactions have been monitored with ligand field spectroscopy. Crystals suitable for X-ray diffraction were obtained for [Ni$_3$(bss)$_4$](BF$_4$)$_2$. The complex crystallizes in the space group $P2_1/c$. The nickel centers are in a square-planar environment; two peripheral nickel centers with an $S_2S'_2$ ($S =$ thiolato; $S' =$ thioether) coordination environment and the central nickel ion with an S_4 coordination environment.

The mononuclear nickel complexes [Ni(bss)$_2$] and [Ni(bsms)$_2$] were reacted with FeCl$_2$, resulting in the hetero-tetranuclear nickel–iron complexes [Ni(bss)$_2$FeCl$_2$]$_2$ and [Ni(bsms)$_2$FeCl$_2$]$_2$. All complexes were characterized by analytical and spectroscopic methods.

Keywords: Nickel; Iron; S ligands; Electronic structure; Ligand field spectroscopy

1. Introduction

Nickel plays an important role in hydrogenases, zureases, carbon-monoxide-dehydrogenase, acetyl-CoA-synthase, superoxide dismutase and methyl-S-coenzyme-M methylreductase. Hydrogenases are widespread among several classes of anaerobic and, occasionally, even aerobic bacteria [1]. These enzymes catalyze the reversible oxidation of dihydrogen, which allows the cell to generate or dispose of reducing equivalents during respiration. In vitro, hydrogenases also catalyze the H^+/D_2 exchange [2].

Hydrogenases can be divided into two main classes, based on their metal content: [NiFe]-hydrogenases and [Fe]-hydrogenases [2]. Extensive studies and characterizations, including single-crystal X-ray diffraction, have revealed the structure of several [NiFe]-hydrogenases [3,4]. The X-ray studies have shown that the active sites of the [NiFe] hydrogenases isolated from *Desulfovibrio gigas* [3] and *D. vulgaris* [4] contain the hetero-dinuclear site [(Cys-S)$_2$Ni^{II}(μ-S-Cys)$_2$Fe^{II}(CN)$_2$(CO)] in which the nickel center has an S_4 coordination sphere. Two cysteines are bridging the nickel center to the iron center. Furthermore, the iron center is coordinated by three diatomic molecules.

In recent years considerable interest has been shown in hydrogenases, because of the fact that possible future energy problems may be solved using a hydrogen economy [5]. This recent interest in hydrogenases is also shown in the variety of structural models published [2,6–12]. However, most of the structural models contain a mixed donor environment around nickel. A variety of

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square-planar nickel complexes have been synthesized with a NiS_4 chromophore [13], and several nickel–iron complexes have been synthesized relevant for hydrogenase modeling [2,11,14–18]. So far only a few heterodimetallic nickel iron complexes have been reported containing an S_4 coordination environment around nickel [16,19]. Recently, we have reported two new nickel complexes with a NiS_4 chromophore, [Ni(xbsms)] and [Ni(bsms)$_2$] [20]. The reactivity of the former nickel complex towards several iron complexes has been investigated, which led to new interesting nickel–iron complexes [19]. In this paper we describe the reactivity towards iron compounds of two nickel complexes with didentate ligands containing one thioether and one thiolate donor, namely [Ni(bsms)$_2$] and [Ni(bss)$_2$] [20], (Hbsms = 2-(benzylsulfanyl)-2-methyl-1-propanethiol, Hbss = 4-mercapto-2-thia-1-butylbenzene). The thiolate donors in these complexes constitute a possible site for further reactivity.

2. Experimental section

2.1. Chemicals

All preparations were carried out in reagent grade solvents. All chemicals used in the syntheses were obtained from Acros or Aldrich and were used without further purification. The complexes were synthesized in an argon atmosphere using standard Schlenk techniques. Solvents were deoxygenated by bubbling through a stream of argon or by the freeze–pump–thaw method and were dried over molecular sieves. The complex [Ni(bsms)$_2$] [20] was synthesized according to published methods.

2.2. Physical measurements

IR spectra were recorded on a Perkin–Elmer FT-IR Paragon 1000 spectrophotometer equipped with a golden gate ATR device, using the reflectance technique (4000–300 cm^{-1}, resolution 4 cm^{-1}). Elemental analyses were carried out on a Perkin–Elmer series II CHNS/O analyzer 2400. Ligand field spectra were obtained on a Perkin–Elmer Lambda 900 spectrophotometer. The diffuse reflectance technique, with MgO as a reference was used for the solid compounds. Ligand field spectra of the solutions were obtained with the used solvent in the reference beam. NMR spectra were taken on a Bruker WM 300 MHz spectrometer and on a Jeol FX-200 Teqmac. Proton and carbon chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). Room temperature magnetic susceptibility measurements were performed on a Johnson Matthey magnetic susceptibility balance type MK1 or with the NMR method [21].

2.3. 2-(benzylthio)ethanol (**1**)

To a solution of benzylmercaptan (10.0 ml, 10.58 g, 0.085 mol) in 50 ml ethanol, was added subsequently, 2-chloroethanol (6.85 g, 0.085 mol) and a solution of NaOH (3.41 g, 0.085 mol) in 25 ml water. After stirring for 1 h and adding an additional amount of water, the product was extracted with 3 × 25 ml chloroform. The combined fractions were washed with 2 × 50 ml water to remove the ethanol. After drying with $MgSO_4$ and filtration, the chloroform was evaporated in vacuo to obtain a yellow oil in a yield of 11.46 g (80%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 6.69 (m, 5H, phenyl ring), 3.12 (s, 2H, Ph–CH_2–S–), 3.06 (t, $^3J = 6.15$ Hz, 2H, S–CH_2–CH_2–OH), 2.33 (s, 1H, –OH), 2.01 (t, $^3J = 6.15$ Hz, 2H, –CH_2–CH_2–OH). δ_C [50.18 MHz, $CDCl_3$, 298 K] 137.80 (Ph–C1), 128.55 (Ph–C2, Ph–C6), 128.26 (Ph–C3, Ph–C5), 126.83 (Ph–C4), 60.13 (–CH_2– CH_2–OH), 35.52 (Ph–CH_2–S–), 33.80 (–S–CH_2–CH_2–).

2.4. {[(2-chloroethyl)thio]methyl}benzene (**2**)

To a solution of **1** (11.46 g, 0.068 mol) in 20 ml chloroform was slowly added a solution of excess thionyl chloride (10 g, 0.085 mol) in 30 ml chloroform. After stirring the reaction mixture for 1 h the chloroform and the excess of thionyl chloride were evaporated in vacuo, to yield 12.76 g of a yellow oil (100%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.24 (m, 5H, phenyl ring), 3.69 (s, 2H, Ph–CH_2–S–), 3.46 (t, $^3J = 7.80$ Hz, 2H, –S–CH_2–CH_2–), 2.70 (t, $^3J = 7.80$ Hz, 2H, –CH_2–CH_2–Cl). δ_C [50.18 MHz, $CDCl_3$, 298 K] 137.31 (Ph–C1), 128.32 (Ph–C2, Ph–C6), 128.17 (Ph–C3, Ph–C5), 126.80 (Ph–C4), 42.44 (Ph–CH_2–S–), 35.99 (–S–CH_2–CH_2–), 32.84 (–CH_2–CH_2–Cl).

2.5. 4-thiouroneum-1-phenyl-2-thiabutane hydrochloride (**3**)

To a solution of **2** (12.76 g, 0.068 mol) in 30 ml ethanol was added a solution of thiourea (5.16 g, 0.068 mol) in 50 ml ethanol. After 5 h of reflux the solvent was evaporated under reduced pressure. Addition of chloroform to the resulting oil induced precipitation of the product as a white solid in a yield of 16.80 g (94%). δ_H [199.56 MHz, DMSO-d6, 298 K] 9.34 (s, 4H, –S–C(NH_2)$_2$ $^+Cl^-$), 7.31 (m, 5H, phenyl ring), 3.83 (s, 2H, Ph–CH_2–S–), 3.46 (t, $^3J = 7.18$ Hz, 2H, –CH_2–CH_2–S–), 2.64 (t, $^3J = 7.18$ Hz, 2H, –S–CH_2–CH_2–). δ_C [50.18 MHz, $CDCl_3$, 298 K] 174.32 (–S–C(NH_2)$_2$ $^+Cl^-$), 142.85 (Ph–C1), 133.57 (Ph–C2, Ph–C6), 133.04 (Ph–C3, Ph–C5), 131.56 (Ph–C4), 39.29 (–S–CH_2–CH_2–), 34.97 (–CH_2–CH_2–S–), 34.47 (Ph–CH_2–S–). IR: ν_{max} (cm^{-1}) = 3037s, 2729m, 1644vs, 1544m, 1495w, 1453m, 1406s, 1301w, 1276w, 1246w, 1117w, 1086w, 931w, 856vw, 815w, 764w, 725m, 704s, 607w, 637vw, 563w, 468m, 390vw.

2.6. 4-Mercapto-2-thia-1-butylbenzene (Hbss) (**4**)

To a solution of **3** (6.0 g, 0.023 mol) in 150 ml water was added a solution of NaOH (1.5 g, 0.038 g) in 10 ml water. The reaction mixture was refluxed for 30 min after which it was cooled to room temperature. Concentrated hydrochloric acid was added until the mixture was neutral. The mixture was extracted with 3×25 ml portions of dichloromethane. The combined fractions were dried over $MgSO_4$. After filtration, the filtrate was evaporated in vacuo to obtain the product as an oil in a yield of 2.65 g (63%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.30 (m, 5H, phenyl ring), 3.73 (s, 2H, Ph–CH_2–S–), 2.63 (m, 4H, –S–CH_2–CH_2–SH), 1.66 (t, 1H, –S*H*). δ_C [50.18 MHz, $CDCl_3$, 298 K] 128.84 (Ph–C2, Ph–C6), 128.72 (Ph–C1) 128.63 (Ph–C3, Ph–C5), 127.20 (Ph–C4), 36.17 (Ph–CH_2–S–), 35.33 (–S–CH_2–CH_2–), 24.43 (–CH_2–CH_2–SH). IR: ν_{max} (cm^{-1}) = 3060s, 3026s, 2919s, 2845s, 2551m, 1950m, 1882m, 1807m, 1759w, 1711vw, 1601s, 1583m, 1493s, 1452s, 1428s, 1273s, 1240s, 1210s, 1136m, 1070s, 1028s, 966m, 947w, 917m, 876w, 844w, 804w, 768s, 700vs, 620w, 564s, 472s, 409vw, 380w.

2.7. [Ni(bss)$_2$] (**5**)

To a solution of Hbss (0.63 g, 3.4 mmol) in 30 ml toluene was added [Ni(acac)$_2$] (0.43 g, 1.7 mmol). After 2 h stirring, the solvent was partly evaporated in vacuo. Upon addition of diethyl ether a brown precipitate was formed, which was collected by filtration in a yield of 0.59 g (81%). δ_H [300.13 MHz, acetone-d6, 298 K] 7.40 (m, 5H, phenyl ring), 4.08 (s, 2H, Ph–CH_2–S–), 2.78 (m, 4H, –S–CH_2–CH_2–S). IR: ν_{max} (cm^{-1}) = 3027w, 2921m, 1601m, 1518w, 1493s, 1452s, 1411s, 1242m, 1194s, 1112s, 1070m, 1026m, 1002w, 941m, 916w, 866w, 838w, 744m, 697vs, 666m, 619m, 564s, 462s, 402s, 352w, 327m. Elemental analysis *Anal.* Calc. for $C_{18}H_{22}NiS_4$ (425.3): C, 50.83; H, 5.21; S, 30.15. Found: C, 49.97; H, 5.35; S, 29.60%.

2.8. [Ni$_3$(bss)$_4$](BF$_4$)$_2$ (**6**)

Method 1: To a solution of Hbss (1.05 g, 5.7 mmol) in 10 ml ethanol was added a solution of $[Ni(H_2O)_6](BF_4)_2$ (1.46 g, 4.3 mmol) in 10 ml ethanol. Immediately the solution turned dark brown and a precipitate was formed. After 30 min stirring the formed brown precipitate was collected by filtration and washed with ethanol. Yield: 1.20 g (78%).

Method 2: To a solution of [Ni(bss)$_2$] (0.17 g, 0.4 mmol) in 30 ml acetone was added a solution of $[Ni(H_2O)_6](BF_4)_2$ (0.070 g, 0.2 mmol) in 15 ml ethanol. After 2 h of stirring, the acetone was evaporated in vacuo to obtain a brown precipitate, which was collected by filtration in a yield of 0.17 g (80%).

Crystals suitable for X-ray diffraction were obtained from acetone/hexane.

IR: ν_{max} (cm^{-1}) = 2998w, 1602w, 1496s, 1456s, 1413s, 1285m, 1242m, 1168m, 1051vs, 1038vs, 1014vs, 994vs, 935s, 880w, 857s, 841m, 766s, 700vs, 678m, 620w, 565m, 520s, 478s, 404w, 377w, 353w, 312w. Elemental analysis *Anal.* Calc. for $C_{36}H_{44}B_2F_8Ni_3S_8$ (1083.3): C, 39.93; H, 4.10; S, 23.68. Found: C, 39.92; H, 4.11; S, 23.16%.

2.9. Ni$_3$(bsms)$_4$](BF$_4$)$_2$ (**7**)

The product can be synthesized in the same two methods as for [Ni$_3$(bss)$_4$](BF$_4$)$_2$. In method 1 the brown product was obtained in a yield of 87%. In method 2 the brown product was obtained in a yield of 82%. δ_H [300.13 MHz, acetone-d6, 323 K] 7.75 (d, $^3J = 7.32$ Hz, 8H, Ph–C2, Ph–C6), 7.51 (m, 12H, Ph–C3, Ph–C4, Ph–C5), 4.32 (d, $^2J = 12.72$ Hz, 4H, Ph–CH*H*–S–), 4.23 (d, $^2J = 12.72$ Hz, 4H, Ph–C*H*H–S–), 2.92 (d, $^2J = 13.14$ Hz, 4H, –C(CH$_3$)$_2$–CH*H*–S), 2.65 (d,$^2J = 13.14$ Hz, 4H, –C(CH$_3$)$_2$–C*H*H–S), 1.69 (s, 12H, –C(CH$_3$)(C*H*$_3$)–), 1.59 (s, 12H, –C(C*H*$_3$) (CH$_3$)–). IR: ν_{max} (cm^{-1}) = 2967w, 1603w, 1496s, 1466m, 1455s, 1420w, 1395w, 1378s, 1368m, 1272w, 1228w, 1199w, 1142m, 1045vs, 1033vs, 929w, 882w, 856w, 815w, 770s, 745s, 721s, 700vs, 620w, 594w, 546w, 519s, 488m, 458s, 409w, 340w. Elemental analysis *Anal.* Calc. for $C_{44}H_{60}B_2F_8Ni_3S_8$ (1193.5): C, 44.22; H, 5.06; S, 21.46. Found: C, 43.42; H, 5.01; S, 21.13%.

2.10. [Ni(bss)$_2$FeCl$_2$]$_2$ (**8**)

To a solution of [Ni(bss)$_2$] (0.080 g, 0.19 mmol) in 30 ml acetonitrile was added solid $FeCl_2 \cdot 4H_2O$ (0.037 g, 0.19 mmol). After 1 h stirring, the acetonitrile was partly evaporated in vacuo until a precipitate was formed. This precipitate was collected by filtration to obtain a brown product in a yield of 0.025 g (24%). IR: ν_{max} (cm^{-1}) = 2980w, 2920w, 1496m, 1455s, 1428m, 1410m, 1277w, 1240m, 1204w, 1156w, 1072m, 1028w, 918m, 840m, 826m, 768s, 700vs, 674s, 628m, 565m, 475s, 352m, 306vs. Elemental analysis *Anal.* Calc.: for $C_{18}H_{22}Cl_2FeNiS_4$ (552.05): C, 39.16; H, 4.02; S, 23.23. Found: C, 38.74; H, 3.90; S, 22.23%.

2.11. [Ni(bsms)$_2$FeCl$_2$]$_2$ (**9**)

To a solution of [Ni(bsms)$_2$] (0.100 g, 0.21 mmol) in 40 ml acetonitrile was added $FeCl_2 \cdot 4H_2O$ (0.041 g, 0.25 mmol). After 1 h of stirring, the unreacted starting products were removed by filtration. The acetonitrile of the filtrate was partly evaporated in vacuo. After adding diethyl ether, the formed precipitate was collected by filtration to obtain a brown product in a yield of 0.045 g (27%). IR: ν_{max} (cm^{-1}) = 2957w, 2922w, 1495m, 1455s, 1418m, 1366m, 1267m, 1245m, 1196m, 1141m, 1082m,

Table 1
Crystal and structure refinement data for the trinuclear nickel complex $[Ni_3(bss)_4](BF_4)_2$ (**6**)

Empirical formula	$C_{36}H_{44}B_2F_8Ni_3S_8$
Molecular weight	1082.96
Crystal dimensions (mm)	0.03 × 0.20 × 0.20
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	19.2282(17)
b (Å)	11.6797(8)
c (Å)	10.0485(17)
β (°)	103.609(7)
V (Å^3)	2193.3(4)
Z	2
$D_{calc.}$ (mg m^{-3})	1.6398(3)
Absorption coefficient μ (mm^{-1})	1.72
Reflections measured	3738
Reflections collected	3027
Reflections observed ($I > 2\sigma(I)$)	1212
R^a	0.0893
$wR_2{}^b$	0.192
S^c	0.975
Number of refined parameters	259

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $w = [\sum^2(F_o) + (0.0594 \times P)^2]^{-1}$.
[c] $S = [\sum w(|F_o|^2 - |F_c|^2)^2/(N_o - N_v)]^{1/2}$.

1070m, 1028w, 1003w, 953w, 919w, 870w, 812w, 781s, 700vs, 620w, 586w, 548w, 481s, 468m, 408w, 383w, 340m, 310s. Elemental analysis *Anal.* Calc. for $C_{22}H_{30}Cl_2FeNiS_4$ (607.2): C, 43.45; H, 4.97; S, 21.09. Found: C, 42.88; H, 4.99; S, 20.40%.

2.12. *Crystal structure determination of* $[Ni_3(bss)_4](BF_4)_2$

X-ray data were collected for a red–brown crystal on an Enraf Nonius TurboCAD4 diffractometer on rotating anode (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å, $T = 150$ K). Reflection profiles were highly structured and only a limited data set up to 23° in could be collected. The structure was solved with Patterson techniques using the program DIRDIF96 [22] and refined on F^2 using SHELXL96 [23]. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Geometrical calculation, including the ORTEP illustration and structure validation were done with PLATON [24]. In Table 1 relevant numerical crystal and refinement data are collected.

3. Results and discussion

3.1. *Synthesis*

The new ligand Hbss was synthesized in an overall yield of 48%. The synthesis of this ligand is similar to the synthesis of Hbsms as described earlier [20]. Starting from this didentate ligand Hbss, two different nickel complexes can be synthesized: the mononuclear complex $[Ni(bss)_2]$ (**5**) and the trinuclear complex $[Ni_3(bss)_4](BF_4)_2$ (**6**). Both the mononuclear and the trinuclear complex are air stable in the solid state. Similarly, $[Ni_3(bsms)_4](BF_4)_2$ (**7**) has been synthesized.

Two new nickel–iron complexes were synthesized: by a reaction of $[Ni(bss)_2]$ or $[Ni(bsms)_2]$ with $FeCl_2$, the complexes $[Ni(bss)_2FeCl_2]_2$ (**8**) and $[Ni(bsms)_2FeCl_2]_2$ (**9**) are formed. Both complexes are moderately air stable and only slightly soluble in polar solvents.

3.2. *Structures of the nickel complexes*

A projection of the structure of the cationic complex $[Ni_3(bss)_4]^{2+}$ is shown in Fig. 1. Crystal data are given in Table 1 and selected bond distances and angles are given in Table 2. $[Ni_3(bss)_4](BF_4)_2$ crystallizes in the space group $P2_1/c$ with two molecules in the unit cell. The structure is trinuclear with the three nickel centers on a row. The central nickel ion, Ni(2) is located on an inversion center and has an S_4 coordination environment consisting of four thiolate sulfurs. The peripheral nickel ions, Ni(1) and Ni(1a) are coordinated by two bss ligands in a *cis* orientation. The overall shape of the trinuclear cation can be described as a zig-zag chain consisting of three square planes. The angle formed between the planes, $Ni(1)S_2S'_2$–$Ni(2)S_4$ is 68.24(19)°. Several compounds have been reported to have a similar structure [10,25–30].

Because of the inversion center Ni(2) has a perfect square-planar surrounding. The peripheral nickel centers have only a small tetrahedral distortion with an interplanar angle of 5.9(2)° between the planes S(6)–Ni(1)–S(9) and S(26)–Ni(1)–S(29). The thiolates are slightly pushed to each other resulting in an angle of only 81.25(17)° for S(6)–Ni(1)–S(26), which is probably due to steric hindrance of the *cis* oriented phenyl groups. The Ni(1)–S–Ni(2) angles of 79.45(15)° and 79.53(17)° together with the Ni–S distances result in a Ni(1)–Ni(2) distance of 2.784(2) Å. In NMR spectroscopy only

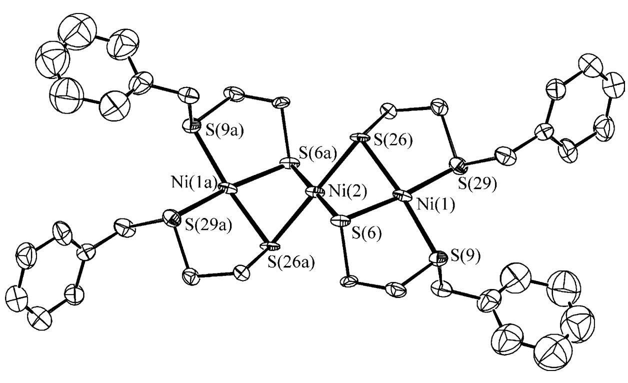

Fig. 1. Displacement ellipsoid plot of $[Ni_3(bss)_4]^{2+}$ (**6**), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) in $[Ni_3(bss)_4]$ $(BF_4)_2$ (**6**)

Ni(1)–S(6)	2.162(5)	Ni(2)–S(6)	2.194(4)
Ni(1)–S(9)	2.196(2)	Ni(2)–S(26)	2.188(5)
Ni(1)–S(26)	2.164(5)	Ni(1)··· Ni(2)	2.784(2)
Ni(1)–S(29)	2.188(5)		
S(6)–Ni(1)–S(9)	92.21(18)	S(6)–Ni(2)–S(26)	80.0(16)
S(6)–Ni(1)–S(26)	81.25(17)	S(6)–Ni(2)–S(26a)	100.0(16)
S(6)–Ni(1)–S(29)	170.90(18)		
S(9)–Ni(1)–S(26)	173.43(19)	Ni(1)–S(6)–Ni(2)	79.45(15)
S(9)–Ni(1)–S(29)	94.75(17)	Ni(1)–S(26)–Ni(2)	79.53(17)
S(26)–Ni(1)–S(29)	91.71(17)		

a = symmetry position $-x, -y, -z$.

broad signals are obtained, indicating paramagnetism, which is probably due to fluxionality of the nickel centers between square planar and tetrahedral.

The structure of $[Ni_3(bsms)_4](BF_4)_2$ (**7**), containing three low-spin Ni(II) centers is expected to be similar to the structure of $[Ni_3(bss)_4](BF_4)_2$, described above. In NMR spectroscopy a clear spectrum is obtained only at 323 K. ^1H NMR shows separate resonances for the protons within a CH_2 group and for the methyl groups on the same carbon atom, confirming a rigid structure of the ligands. Only the phenyl groups have no hindrance in rotating, as only three signals are observed for each phenyl group.

The complex $[Ni(bss)_2]$ (**5**), containing a low-spin Ni(II) center, is expected to be similar to the structure of $[Ni(bsms)_2]$ with both ligands in *trans* positions [20].

3.3. Reactivity of the mononuclear complexes

The reactions of $[Ni(bss)_2]$ and $[Ni(bsms)_2]$ with $Ni(BF_4)_2$ to form the trinuclear complexes can be followed in ligand field spectroscopy. In Fig. 2 the titration curve of the reaction of $[Ni(bss)_2]$ with $Ni(BF_4)_2$ is shown. The titration curve for $[Ni(bsms)_2]$ is very similar. As can be observed in Fig. 2, the maximum change is reached at 0.5 equivalents of $Ni(BF_4)_2$, confirming the symmetrical structure of two Ni(1) centers and one Ni(2) center. The several isosbestic points show that no intermediate species is observed and the formation of the trinuclear complex is instantaneous. The parent mononuclear nickel complexes can be formed again in a reaction of the trinuclear complexes with 1,10-phenanthroline, resulting in half an equivalent of side product $[Ni(phen)_3](BF_4)_2$.

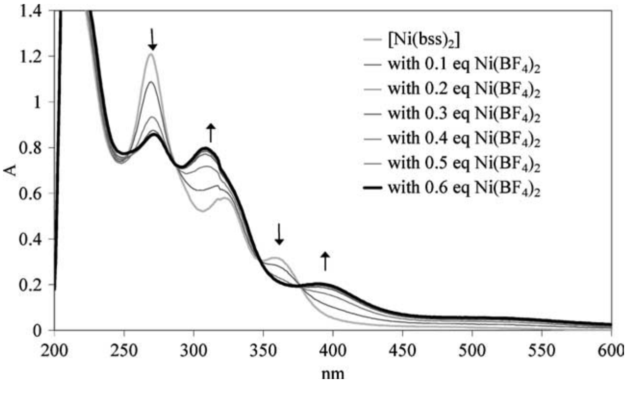

Fig. 2. Titration curve of $[Ni(bss)_2]$ with $[Ni(BF_4)_2]$ yielding $[Ni_3(bss)_4]$ $(BF_4)_2$ in acetone.

The reactivity of the mononuclear complexes to form the linear trinuclear complexes comprises a rearrangement of the ligands from *trans* to *cis*. Thus, despite the *trans* orientation of the didentate ligands in the mononuclear nickel complexes these may still be useful in the pursuit for hetero-dinuclear nickel–iron complexes.

3.4. Structures of the nickel–iron complexes

The structures of $[Ni(bss)_2FeCl_2]_2$ (**8**) and $[Ni(bsms)_2FeCl_2]_2$ (**9**) are expected to be similar to $[Ni(xbsms)FeCl_2]_2$ based on elemental analysis and IR [19]. Room temperature magnetic susceptibility experiments show that the iron centers are high spin, with a μ_{eff} of 4.20 per iron center for **8** and a μ_{eff} of 4.35 per iron for **9**. These values are lower than that reported for $[Ni(xbsms)FeCl_2]_2$ ($\mu_{eff} = 5.35$) [19].

3.5. UV–Visible–NIR spectroscopy of the complexes

The square-planar surrounding of the nickel centers in all of the complexes is reflected in their ligand field spectra. The data are presented in Table 3 for the nickel complexes and in Table 4 for the nickel–iron complexes. All complexes are brown solids and yield pale brown solutions in acetonitrile, acetone or chloroform. For $[Ni(bss)_2]$ all absorption bands are similar to the absorption bands of the comparable complex $[Ni(bsms)_2]$ [20].

Only small differences in absorption maxima between a solution in acetone and a solution in acetonitrile are observed, which excludes solvent coordination. Due to d–d transitions three absorption bands are found, between 13,000 and 26,000 cm^{-1}. Compared to the mononuclear complexes, for the trinuclear complexes an extra absorption band is observed around 24,000 cm^{-1}

Table 3
Electronic absorption maxima for the Ni(II) complexes

	ν/cm^{-1} (ε/mol^{-1} l cm^{-1})			
	Solid state[a]	Acetone	Acetonitrile	Chloroform
[Ni(bss)$_2$]	17,200		14,900 (99)	14,700 (62)
	22,700		21,600 (sh)	22,100 (sh)
	27,200		28,200 (5159)	28,300 (8087)
	32,900		31,400 (8799)	31,400 (11,500)
	38,000			
[Ni$_3$(bss)$_4$](BF$_4$)$_2$	13,300	13,200 (217)	13,100 (287)	
	19,000	19,800 (2172)	19,800 (2163)	
	23,400	25,600 (9037)	25,600 (10,306)	
	30,200			
	36,700		36,100 (84,817)	
[Ni$_3$(bsms)$_4$](BF$_4$)$_2$	13,800		13,400 (224)	
	19,300	20,200 (3904)	20,200 (1879)	
	22,900	23,200 (9059)	25,600 (7943)	
	29,800		32,400 (28,683)	
	36,700		36,700 (29,240)	

[a] Diffuse reflectance.

Table 4
Electronic absorption maxima for the Ni(II)–Fe(II) complexes

	ν/cm^{-1} (ε /mol^{-1} l cm^{-1})		
	Solid state[a]	Acetonitrile	Chloroform
[Ni(bss)$_2$FeCl$_2$]$_2$(**8**)	16,200		
	19,300	20,000 (sh)	18,200 (1191)
	24,500	26,500 (sh)	24,200 (2861)
	30,200	33,500 (sh)	30,800 (11,400)
	36,700		
[Ni(bsms)$_2$FeCl$_2$]$_2$(**9**)		13,600 (116)	13,800 (sh)
	19,500	20,000 (sh)	19,300 (1287)
	21,000		
	23,900		24,200 (sh)
		27,900 (sh)	27,500 (sh)
	35,500	33,400 (13,685)	30,600 (sh)
		38,000 (13,660)	37,300 (17,199)

[a] Diffuse reflectance.

arising from the extra nickel center. This absorption band is at high energy due to the four electron-donating thiolate sulfurs. The absorption maxima of the d–d transitions of Ni(1) and Ni(1a) have shifted to lower energy, around 13,500 and 20,000 cm^{-1}, due to the bridging and therefore less electron-rich thiolate sulfurs.

The ligand field spectra of the [NiL$_2$FeCl$_2$]$_2$ complexes **8** and **9** are similar to the ligand field spectrum of [Ni(xbsms)FeCl$_2$]$_2$, suggesting a similar hetero-tetranuclear structure [19]. The absorption maxima resulting from ligand to metal charge transfer are different for a solution in chloroform as compared with a solution in acetonitrile, indicating possible coordination of MeCN.

4. Conclusions and outlook

Three new nickel complexes have been synthesized, the mononuclear complex [Ni(bss)$_2$], and the trinuclear nickel complexes [Ni$_3$(bss)$_4$](BF$_4$)$_2$ and [Ni$_3$(bsms)$_4$](BF$_4$)$_2$. The reactivity of the complexes is shown in the *trans* to *cis* rearrangement of the ligands. Furthermore, two new nickel iron complexes have been synthesized, starting from both mononuclear complexes in a reaction with FeCl$_2$. These nickel–iron complexes show similar behavior compared to the nickel–iron complexes with the ligand xbsms [19].

The synthesized compounds have been made in a search for new structural models of [NiFe]-hydrogenases. In a subsequent study, the complexes will be screened for hydrogenase-like activity by means of reaction of the [NiFe]-complexes with dihydrogen or protons.

5. Supporting information

The crystallographic data have been deposited with the Cambridge Crystallographic Data Base, CCDC no

220724. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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