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FULL PAPER

Synthesis, characterisation and crystal structures of new nickel complexes in S_4 coordination spheres; an unprecedented rearrangement during ligand synthesis

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Two new nickel(II) complexes were synthesized with an S_4 coordination environment. These complexes were synthesized by *in situ* deprotection of thiouronium salts in the presence of nickel(II). The ligands used are 4-mercapto-3,3-methyl-1-phenyl-2-thiabutane (Hbsms) and α,α′-bis(4-mercapto-3,3-methyl-2-thiabutyl)-*o*-xylene (H_2xbsms). The former is a didentate ligand containing one thioether and one thiolate group and the latter is a dithioether dithiolate tetradentate ligand. The differences between these ligands upon coordination to nickel have been investigated. During the synthesis of these ligands, an unprecedented spontaneous rearrangement occurs, which is very fast and selective to a single product. The complexes were characterized by analytical, spectroscopic and electrochemical methods. The geometry of the nickel complexes is square planar according to the single-crystal X-ray structures. In [Ni(bsms)$_2$] the two ligands are coordinated with the thiolates in *trans* positions towards each other; in [Ni(xbsms)] the thiolates are in enforced *cis* positions. [Ni(bsms)$_2$] crystallizes in the triclinic space group $P\bar{1}$ and has one centrosymmetric molecule in the unit cell. [Ni(xbsms)] crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules in the asymmetric unit, however, the differences between these two molecules are very small. The Ni–S distances are 2.1730(4)–2.1909(6) Å and in the common range for thiolates and chelating thioethers.

Introduction

Hydrogenases are widespread among several classes of anaerobic and occasionally aerobic bacteria.[1] These enzymes catalyse the reversible oxidation of dihydrogen. Furthermore, *in vitro* they have been shown to catalyse the H^+/D_2 exchange. Extensive studies and characterizations, including single-crystal X-ray diffraction, have revealed the structure of several Fe-only and [NiFe]-hydrogenases.[2–6] The X-ray studies have shown that the active sites of the [NiFe] enzymes isolated from *Desulfovibrio gigas* and *Desulfovibrio vulgaris* contain the heterodinuclear site [(Cys–S)$_2$Ni(μ-S–Cys)$_2$Fe(CN)$_2$(CO)]. In the last few years, considerable interest has been shown in the [NiFe]-hydrogenases and their structural modelling.[7–16] Most of the synthetic models contain a mixed-donor environment and only a few square-planar nickel complexes have been synthesized which contain only sulfur donors in the coordination environment.[17–21] With this information, it was decided to synthesize nickel complexes with an S_4-donor environment, incorporating two thiolate sulfur donors and two thioether sulfur donors. With Ni(II) this results in a neutral complex, with the thiolate sulfurs being available to bridge to *e.g.* an iron centre. The present paper describes two new nickel complexes with new chelating ligands. The ligands designed for this study are 4-mercapto-4-methyl-1-phenyl-2-thiapentane and α,α′-bis(3-mercapto-3-methyl-1-thiabutyl)-*o*-xylene. A schematic drawing of the intended ligands is shown in Fig. 1. The methyl groups on the carbon α to the thiolate groups are intended to prevent oligomerisation of the nickel complexes.

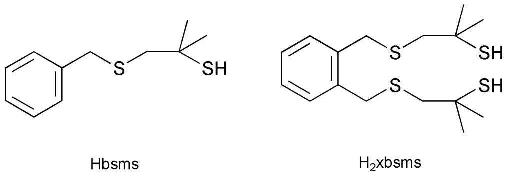

Fig. 1 Schematic drawing of the target ligands.

Results and discussion

Synthesis

The new ligands reported here were synthesized in a good overall yield of 70% for both ligands. A schematic drawing of the synthesis of the ligands is shown in Scheme 1. During the ligand synthesis a spontaneous rearrangement takes place, by which the methyl groups on the α carbon end up at the β positions. This rearrangement clearly takes place during the reaction of the hydroxyl group with thionyl chloride, *via* a proposed mechanism shown in Scheme 2, which includes episulfonium salt (**2A**) as a possible intermediate. After the formation of the episulfonium salt, the chloride will attack the least sterically hindered carbon,[22] thus selectively opening the ring to form **2** and **7**. As this reaction is very fast **2** and **7** are the kinetically most favourable products.

To the best of our knowledge this spontaneous rearrangement is unprecedented. In fact a few reports on the deliberate synthesis of episulfonium salts have been published. One of these describes the use of a silver salt to abstract chloride ions to facilitate the formation of the episulfonium salt;[23] another report describes the use of very low temperatures to isolate the episulfonium salt.[24] The spontaneous rearrangement described here takes place under ambient conditions without the use of silver salts. The reaction apparently is very rapid, only the final products **2** and **7** are obtained and the intermediate episulfonium salts are not observed. The chlorides in **2** and **7** are not strongly bound, which has been confirmed by the reaction of **2** with $AgNO_3$, yielding an immediate precipitate of AgCl.

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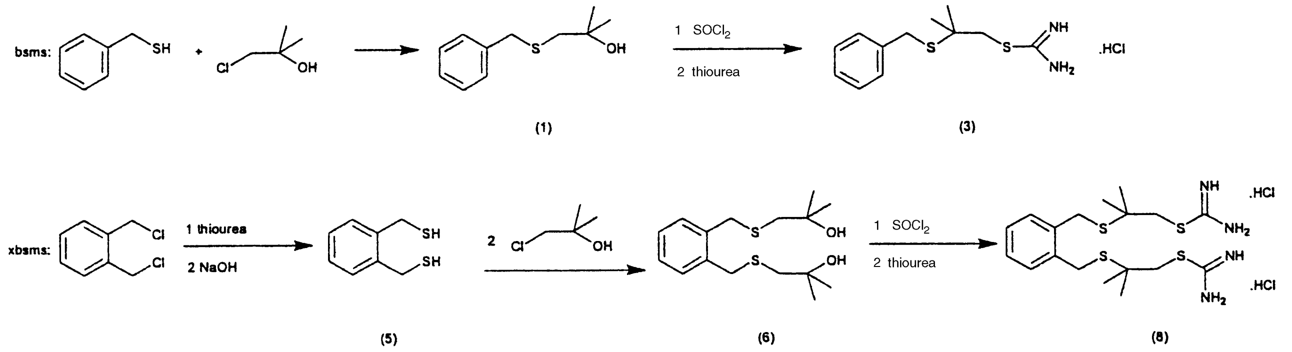
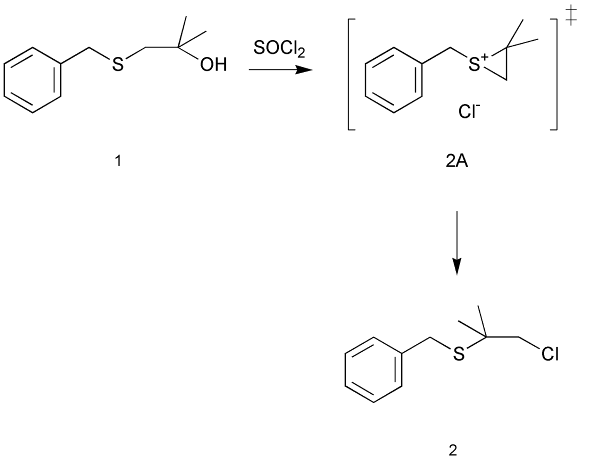


Scheme 1 Synthesis of the thiouronium salt ligands.



Scheme 2 Proposed rearrangement mechanism of the ligands.

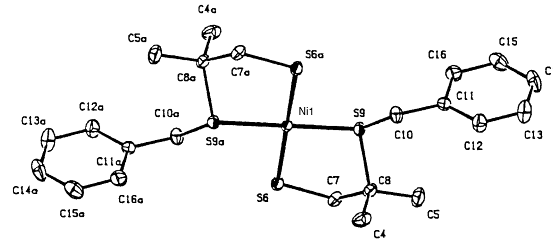


Fig. 2 Displacement ellipsoid plot of Ni(bsms)$_2$, drawn at the 50% probability level. Symmetry operation a: $-x, 1 - y, 1 - z$.

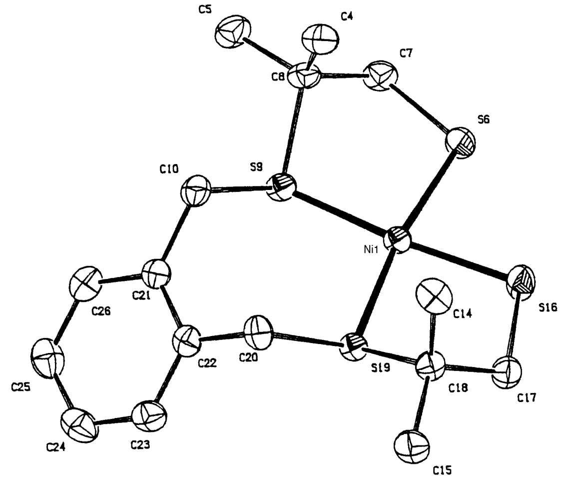


Fig. 3 Displacement ellipsoid plot of molecule 1 of Ni(xbsms), drawn at the 50% probability level.

NOESY NMR has been used to confirm the description of **2** and **7** as the rearranged products with the methyl groups on the β carbon atom.

Although the thiol ligands are quite stable in an oxygen atmosphere and only oxidize after several days, during deprotection some disulfide is also formed. This is probably due to the basic conditions used during the deprotection of the thiourea derivatives.

The nickel complexes were synthesized by reactions of [Ni(acac)$_2$] with the thiouronium precursor salts of the ligands, **3** and **8** respectively, in ethanol in the presence of the base tetramethylammonium hydroxide. The hydroxide ion attacks at the thiouronium carbon atom resulting in urea and a thiolate ligand, which then coordinates to the nickel centre. The [Ni(acac)$_2$] does not dissolve well in ethanol, but after refluxing the complex is formed. The complex [Ni(xbsms)] was formed directly in pure form. The complex [Ni(bsms)$_2$] needs recrystallisation from ethanol to remove the tetramethylammonium salt impurities. By the use of the thiouronium salts of the ligands and the *in situ* formation of the thiolate ligand, the isolation of the oxidation sensitive thiol-ligands is circumvented. The complexes were synthesized and handled in an inert atmosphere, but were found to be stable in the solid state in air for several days.

Structures of [Ni(xbsms)] and [Ni(bsms)$_2$]

Projections of the structures of the complexes [Ni(bsms)$_2$] and [Ni(xbsms)] are shown in Figs. 2 and 3 respectively. Crystal data are given in Table 1 and selected bond distances and angles are given in Table 2.

[Ni(bsms)$_2$] crystallizes in the space group $P\bar{1}$ with one molecule in the unit cell, the nickel ion residing on an inversion center. The complex contains a Ni(II) centre in square-planar surroundings. The nickel ion has a coordination environment which consists of two thiolate donors and two thioether groups. The thiolates are coordinated *trans* to each other. The bond distances of thiolate sulfur to nickel are 2.1903(4) Å and the bond distances of the thioether sulfur to nickel are 2.1730(4) Å. The bite-angle of the ligand, S6–Ni–S9 is 88.127(16)°, which is only slightly less than the ideal 90°. Due to the inversion centre at the nickel ion, the environment around nickel is perfectly planar. Stacking of aromatic rings or hydrogen bonding is not observed between the molecules in the lattice.

[Ni(xbsms)] crystallizes in the space group $P2_1/c$ and has two independent molecules in the asymmetric unit. However, the differences between the two molecules are very small, so only one of them is discussed here. The complex contains a Ni(II) centre which is in square-planar surroundings with an $S_2S'_2$ coordination sphere. Two thiolate donors and two thioether groups are coordinated to the nickel centre, and are in enforced *cis* positions. The bond distances of the thiolate sulfurs to nickel are 2.1802(6) and 2.1869(6) Å. The bond distances of the thioether sulfurs to nickel are 2.1909(6) and 2.1756(5) Å. The angles in this complex differ from the ideal angles 90 and 180°. The angle of S6–Ni–S9 and S16–Ni–S19 are 87.92(2)° and 87.11(2)°. These angles are slightly less than the ideal 90°, due to the limitations of the 5-membered rings. However, the 7-

Table 1 Crystal and structure refinement data for the nickel complexes [Ni(bsms)$_2$] and [Ni(xbsms)]

	[Ni(bsms)$_2$]	[Ni(xbsms)]
Empirical formula	$C_{22}H_{30}NiS_4$	$C_{16}H_{24}NiS_4$
Molecular weight	481.43	403.30
Crystal dimensions/mm	0.24 × 0.24 × 0.18	0.32 × 0.12 × 0.12
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$
a/Å	7.1006(2)	13.2008(2)
b/Å	8.3936(2)	17.3926(2)
c/Å	10.4298(4)	20.6855(2)
α/°	108.6417(16)	90
β/°	105.6636(17)	129.5047(7)
γ/°	89.9694(19)	90
V/Å^3	564.61(3)	3664.44(9)
Z	1	8
D_{calc}/Mg m^{-3}	1.416	1.462
μ/cm^{-1}	12.3	15.06
Reflections measured	6230	65338
Reflections collected	2670	8398
Reflections observed [$I > 2\sigma(I)$]	2283	6460
R^a	0.0308	0.0311
$R_w{}^b$	0.0679	0.0685
S^c	1.056	1.010
No. of refined parameters	126	387

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = \sigma^{-2}F^{-1}$. ^{c} $S = [\Sigma(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for [Ni(xbsms)] and [Ni(bsms)$_2$]

	[Ni(bsms)$_2$]	[Ni(xbsms)] (molecule 1)
Ni1–S6	2.1903(4)	2.1802(6)
Ni1–S9	2.1730(4)	2.1909(6)
Ni1–S16		2.1869(6)
Ni1–S19		2.1756(5)
S6–Ni1–S9	88.127(16)	87.92(2)
S6–Ni1–S16(S6a)	180	84.05(2)
S6–Ni1–S19(S9a)	91.874(16)	170.72(2)
S9–Ni1–S16		171.45(2)
S9–Ni1–S19(S9a)	180	100.75(2)
S16–Ni1–S19		87.11(2)

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

	ν/cm^{-1} (ε/mol^{-1} l cm^{-1})		
	Solid state	Chloroform	Acetonitrile
[Ni(bsms)$_2$]		14 400 (96)	14 800 (sh)
	21 500	22 000 (sh)	22 000 (sh)
			28 200 (6500)
			32 400 (sh)
			35 000 (13000)
	39 300		38 000 (16000)
[Ni(xbsms)]	15 300	15 600 (69)	15 700 (67)
	23 200	19 800 (sh)	19 700 (sh)
	29 400	25 600 (sh)	30 200 (6300)
	35 500		34 400 (16000)

membered ring enforces an angle of 100.75(2)° for S9–Ni–S19 and therefore pushes the thiolates together, resulting in an angle of only 84.05(2)° for S6–Ni–S16. Also due to this tetradentate coordination mode, the [Ni(xbsms)] complex has a small tetrahedral distortion with a dihedral angle of 4.31(4)° as defined by the planes S6–Ni1–S9 and S16–Ni1–S19. No stacking or hydrogen bonding is observed between the molecules in the lattice.

Both complexes show no remarkable differences in bond distances and angles compared to complexes from the literature.[25] The bond distances of the thioether sulfur and the thiolate sulfur to the nickel ion are unexceptional.[19]

NMR and UV–Visible–NIR spectroscopy of [Ni(bsms)$_2$] and [Ni(xbsms)]

The square-planar surroundings of both nickel centres is also shown in their ligand field spectra. Both complexes remain square planar in solution with at best a slight tetrahedral distortion, which is also shown by NMR spectroscopy. Because of this tetrahedral distortion, the NMR signals of the complexes dissolved in chloroform are slightly broadened.

Electronic spectra of the complexes were recorded using diffuse reflection methods and as solutions in chloroform and acetonitrile. The data are presented in Table 3. The complex [Ni(bsms)$_2$] is a brown solid and yields orange solutions in chloroform and acetonitrile, whereas the [Ni(xbsms)] complex is a dark green solid and yields green solutions in chloroform and acetonitrile. Two absorption bands due to d–d transitions are found between 14 000 cm^{-1} and 24 000 cm^{-1}, which are characteristic of square-planar nickel complexes with a NiS_4 chromophore. Only small differences are observed between the chloroform and acetonitrile solutions, indicating that MeCN does not coordinate to the nickel centres. Around 15 000 cm^{-1}, [Ni(bsms)$_2$] shows an absorption maximum at lower energy than [Ni(xbsms)], while around 22 000 cm^{-1} the former shows an absorption maximum at higher energy than the latter. In [Ni(bsms)$_2$] no absorption maximum is found around 25 000 cm^{-1}. The absorption maxima at 25 000 cm^{-1} and higher are due to LMCT transitions. In chloroform, these absorption maxima are hidden underneath the strong absorptions from the solvent.

Electrochemical results

The electrochemical behaviour of both nickel complexes was investigated using cyclic voltammetry. The experiments were performed in acetonitrile between 1.7 and −1.8 V *vs.* an Ag/AgCl reference electrode. At a scan rate of 0.20 V s^{-1} only irreversible reduction and oxidation waves are observed for both [Ni(xbsms)] and [Ni(bsms)$_2$]. [Ni(xbsms)] shows irreversible oxidation waves at 1406 and 508 mV. [Ni(bsms)$_2$] shows irreversible oxidation waves at 1030 and 522 mV. This implies that the Ni(III) state is inaccessible for both complexes, although it is generally accepted that thiolate ligands stabilize higher oxidation states. Furthermore, both complexes only show irreversible reduction waves at −508 and −1572 mV for [Ni(xbsms)] and −762 and −1465 mV for [Ni(bsms)$_2$]. Because of the presence of non-innocent thiolate and thioether donors, the exact nature of the redox sites cannot be established using these data. However, this was not investigated further. Other techniques would be needed.

Conclusions

Two new nickel complexes were synthesized both in an S_4 coordination environment. These complexes are promising for new structural models for [NiFe]-hydrogenases. The thiolates can form a bridge between nickel and iron upon coordinating to an iron complex. The [Ni(xbsms)] complex has the advantage that only one side of the molecule is available for a reaction with an iron complex, while the thiolates are in a *cis* orientation and are ideal to bridge to an iron centre. Two new ligands were synthesized. During the synthesis of these ligands, an unprecedented spontaneous rearrangement occurred, which is very fast and selective to one product. Further studies will deal with the synthesis of nickel–iron complexes for better understanding of [NiFe]-hydrogenases.

Experimental

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 unless mentioned otherwise. The nickel 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 methods and were dried over molecular sieves. The complex [Ni(acac)$_2$] was synthesized according to published methods.[26]

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 analyser 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. Chemical shifts are indicated in ppm relative to tetramethylsilane (TMS). The electrochemistry measurements were performed with an Autolab PGstat10 potentiostat controlled by GPES4 software. A three-electrode system was used, consisting of a platinum working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode. The experiments were carried out in acetonitrile at room temperature in an argon atmosphere with tetrabutylammonium hexafluorophosphate (0.10 M) as electrolyte. Under these conditions the ferrocenium–ferrocene couple is located at +430 mV with a peak-to-peak separation of 59 mV. All potentials are reported relative to Ag/AgCl. Mass experiments were performed on a Finnigan MAT 900 equipped with an electrospray interface. Spectra were collected by constant infusion of the sample dissolved in methanol/water with 1% HOAc.

Syntheses

4-Hydroxy-4-methyl-1-phenyl-2-thiapentane (1). Benzylmercaptan (12.40 g, 0.1 mol) and 1-chloro-2-methyl-2-propanol (10.85 g, 0.1 mol) were dissolved in 15 ml ethanol. While cooling the mixture on ice, a solution of NaOH (4.05 g, 0.1 mol in 6 ml H_2O) was slowly added. After two hours stirring at room temperature, the formed NaCl was removed by filtration. After evaporating the ethanol under reduced pressure, water was added and the product was extracted with chloroform. The combined chloroform layers were dried with $MgSO_4$ and evaporated and a yellow oil was obtained in a yield of 14.46 g (74%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.31 (m, 5H, phenyl ring), 3.78 (s, 2H, Ph–CH_2–S–), 2.58 (s, 2H, –S–CH_2–C(CH$_3$)$_2$–OH), 2.25 (s, 1H, –OH), 1.25 (s, 6H, CH_3). δ_C [50.18 MHz, $CDCl_3$, 298 K] 138.00 (Ph–C1), 128.75 (Ph–C2), 128.34 (Ph–C3), 126.91 (Ph–C4), 70.49 –C(CH$_3$)$_2$–), 45.39 (–S–CH$_2$–C-(CH$_3$)$_2$–OH), 38.00 (Ph–CH$_2$–S–), 28.57 (CH$_3$).

4-Chloro-3,3-dimethyl-1-phenyl-2-thiabutane (2). To a solution of **1** (14.46 g, 0.074 mol) in 20 ml chloroform was slowly added a solution of excess thionyl chloride (20 g, 0.17 mol) in 30 ml chloroform. After an hour stirring the chloroform and excess thionyl chloride were evaporated under reduced pressure, to yield 15.83 g of a yellow oil (100%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.33 (m, 5H, phenyl ring), 3.83 (s, 2H, Ph–CH_2–S–), 2.86 (s, 2H, S–C(CH$_3$)$_2$–CH_2–Cl), 1.63 (s, 6H, CH_3). δ_C [50.18 MHz, $CDCl_3$, 298 K] 137.80 (Ph–C1), 128.84 (Ph–C2), 128.34 (Ph–C3), 126.97 (Ph–C4), 70.14 (–C(CH$_3$)$_2$–) 46.53 (–S–C(CH$_3$)$_2$–CH$_2$–Cl), 38.03 (Ph–CH$_2$–S–), 31.35 (CH$_3$).

4-Thiouronium-3,3-dimethyl-1-phenyl-2-thiabutane hydrochloride (3). To a solution of **2** (15.83 g, 0.074 mol) in 30 ml ethanol was added a solution of thiourea (5.61 g, 0.074 mol) in 60 ml ethanol. After 5 hours of reflux the solvent was evaporated under reduced pressure, which resulted in a solid. This solid was washed with a small amount of ethanol and diethyl ether to obtain a white product in a yield of 18.41 g (95%). δ_H [199.56 MHz, DMSO-d6, 298 K] 9.35 (s, 4H, –S–C(NH_2)$_2$$^+Cl^-$), 7.30 (m, 5H, phenyl ring), 3.81 (s, 2H, Ph–CH_2–S–), 3.58 (s, 2H, –S–C(CH$_3$)$_2$–CH_2–), 1.33 (s, 6H, CH_3). δ_C [50.18 MHz, [d6]-DMSO, 298 K] 170.30 (–S–C(NH$_2$)$_2$$^+Cl^-$), 137.66 (Ph–C1), 129.02 (Ph–C2), 128.41 (Ph–C3), 126.89 (Ph–C4), 45.83 (–C(CH$_3$)$_2$–CH$_2$–), 42.33 (–S–C(CH$_3$)$_2$–CH$_2$–), 32.32 (Ph–CH$_2$–S–), 27.50 (CH$_3$).

4-Mercapto-3,3-methyl-1-phenyl-2-thiabutane (Hbsms). One equivalent NaOH was added to a solution of **3** (0.38 g, 1.33 mmol) in 50 ml water. After 15 minutes stirring at room temperature, the mixture was acidified with a concentrated HCl solution to pH 7. The product was then extracted with 3 portions of 20 ml chloroform. The combined extracts were dried over $MgSO_4$. After filtration the solvent was evaporated under reduced pressure resulting in a yellow oil. δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.33 (m, 5H, Ph), 3.73 (s, 2H, Ph–CH_2–S–), 2.71 (d, ^3J = 8.4 Hz, 2H, C(CH$_3$)$_2$–CH_2–SH), 1.62 (t, ^{3}J = 8.4 Hz, 1H, –SH), 1.39 (s, 6H, CH_3). δ_C [50.18 MHz, $CDCl_3$, 298 K] 137.77 (Ph–C1), 128.72 (Ph–C2), 128.32 (Ph–C3), 126.77 (Ph–C4), 46.91 (–S–C(CH$_3$)$_2$–), 37.01 (–C(CH$_3$)$_2$–CH$_2$–SH), 32.98 (Ph–CH$_2$–S–), 27.03 (CH$_3$). The product contained varying amounts of the disulfide as characterized with δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.33 (m, 5H Ph), 3.78 (s, 2H, Ph–CH_2–S–), 3.10 (s, 2H, C(CH$_3$)$_2$–CH_2–S–S–), 1.41 (s, 6H, CH_3). δ_C [50.18 MHz, $CDCl_3$, 298 K] 54.17 (–C(CH$_3$)$_2$–CH$_2$–S–S–), 46.20 (–C(CH$_3$)$_2$–), 33.22 (Ph–CH$_2$–S–), 27.67 (CH$_3$).

α,α′-Dithiouronium-*o*-xylene dihydrochloride (4). To a solution of α,α′-dichloro-*o*-xylene (5.0 g, 28.5 mmol) in 25 ml ethanol was added a solution of thiourea (4.34 g, 57.1 mmol) in 50 ml ethanol. After 30 min refluxing a white product was formed. After filtration and washing with ethanol and diethyl ether the yield was 8.48 g (91%). δ_H [199.56 MHz, D_2O, 298 K] 7.54 (m, 4H, phenyl ring), 4.80 (s, –S–C(NH_2)$_2$$^+Cl^-$ and H_2O), 4.59 (s, 4H, Ph–CH_2–S–).

α,α′-Dimercapto-*o*-xylene (5). To a solution of **4** (8.48 g, 25.9 mmol) in 50 ml water was added a solution of NaOH (3.11 g, 78.0 mmol) in 20 ml water. After 3 hours refluxing the mixture was neutralized with a concentrated HCl solution. The product was extracted with dichloromethane. The combined organic layers were dried with $MgSO_4$ and evaporated under vacuum to yield 4.03 g of a solid off-white product (91%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.31 (m, 4H, phenyl ring), 3.88 (d, ^3J = 7.2 Hz, 4H, –CH_2–), 1.89 (t, ^3J = 7.2 Hz, 2H, –SH). δ_C [50.18 MHz, $CDCl_3$, 298 K] 138.50 (Ph–C1, Ph–C2), 129.54 (Ph–C3, Ph–C6), 127.70 (Ph–C4, Ph–C5), 25.95 (–$C$$H_2$–).

α,α′-Bis(3-hydroxy-3-methyl-1-thiabutyl)-*o*-xylene (6). In 80 ml ethanol **5** (3.59 g, 21.1 mmol) and 1-chloro-2-methyl-2-propanol (4.58 g, 42.2 mmol) were dissolved. While cooling on ice, a solution of NaOH (1.68 g, 42.2 mmol) in 10 ml water was added. After one hour stirring, the product was worked up in a similar way as described for **1**, resulting in a yellow oil in a yield of 6.62 g (100%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.26 (m, 4H, phenyl ring), 3.98 (s, 4H, Ph–CH_2–S–), 2.66 (s, 4H, –S–CH_2–C$(CH_3)_2$–), 2.38 (s, 2H, OH), 1.28 (s, 12 H, CH_3). δ_C [50.18 MHz, $CDCl_3$, 298 K] 135.96 (Ph–C1, Ph–C2), 130.30 (Ph–C3, Ph–C6), 127.03 (Ph–C4, Ph–C5), 70.52 (–CH_2–$C$$(CH_3)_2$–OH), 45.59 (–S–$C$$H_2$–C$(CH_3)_2$–OH), 35.17 (Ph–$C$$H_2$–S–), 28.37 ($C$$H_3$).

α,α′-Bis(3-chloro-2,2-methyl-1-thiapropyl)-*o*-xylene (7). The product was synthesized in the same way as **2**, resulting in a yellow oil in a yield of 7.40 g (100%). δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.26 (m, 4H, phenyl ring), 4.02 (s, 4H, Ph–CH_2–S–), 2.90 (s, 4H, –S–C$(CH_3)_2$–CH_2–Cl), 1.62 (s, 12 H, CH_3). δ_C [50.18 MHz, $CDCl_3$, 298 K] 136.02 (Ph–C1, Ph–C2), 130.71 (Ph–C3, Ph–C6), 127.44 (Ph–C4, Ph–C5), 70.23 (–S–$C$$(CH_3)_2$–$CH_2$–Cl), 47.34 (–S–C$(CH_3)_2$–$C$$H_2$–Cl), 35.64 (Ph–$C$$H_2$–S–), 31.41 ($C$$H_3$).

α,α′-Bis(3-thiouronium-2,2-methyl-1-thiapropyl)-*o*-xylene dihydrochloride (8). The product was synthesized in the same way as **4**, resulting in a white solid in a yield of 9.05 g (85%). δ_H [199.56 MHz, D_2O, 298 K] 7.36 (m, 4H, phenyl ring), 4.80 (s, –S–C$(NH_2)_2^+Cl^-$ and H_2O), 4.05 (s, 4H, Ph–CH_2–S–), 3.48 (s, 4H, –S–C$(CH_3)_2$–CH_2–), 1.54 (s, 12 H, CH_3).

α,α′-Bis(3-mercapto-2,2-methyl-1-thiapropyl)-*o*-xylene (H_2xbsms). This reaction was performed in a similar manner to that of Hbsms, except that this reaction was performed in an inert atmosphere preventing thiol oxidation to disulfide. δ_H [199.56 MHz, $CDCl_3$, 298 K] 7.23 (m, 4H, phenyl ring), 3.86 (s, 4H, Ph–CH_2–S–), 2.79 (d, ^3J = 8.2 Hz, 4H, –C$(CH_3)_2$–CH_2–SH), 1.66 (t, ^3J = 8.2 Hz, 2H, –SH), 1.42 (s, 12H, CH_3).

[Ni(bsms)$_2$]. To a suspension of [Ni(acac)$_2$] (0.52 g, 2.02 mmol) in 35 ml ethanol was added two equivalents of **3** (1.18 g, 4.05 mmol). After the addition of two equivalents of NMe_4OH (0.73 g, 4.05 mmol), the solution was refluxed for 2 hours. The formed crude brown product was collected by filtration and purified by refluxing for 1 hour in 15 ml ethanol to remove additional amounts of impurities. The product was isolated and dried under vacuum to yield 0.58 g (60%) of a brown powder. Crystals suitable for X-ray diffraction were obtained from the filtrate upon standing. δ_H [300.13 MHz, $CDCl_3$, 300 K] 7.36 (d ^3J = 6.9 Hz, 4H, Ph–C2, Ph–C6), 7.20 (m, 6H, Ph–C3, Ph–C4, Ph–C5), 4.02 (s, 4H, Ph–CH_2–S–), 2.31 (s, 4H, C$(CH_3)_2$–CH_2–S–), 1.35 (s, 12H, CH_3). ν_{max}/cm^{-1} = 2960w, 2908m, 1495m, 1454m, 1406m, 1382m, 1364m, 1261m, 1196w, 1140m, 1081m, 1029w, 954w, 916w, 892w, 858m, 756m, 698s, 599w, 499w, 461s, 391s, 326w cm^{-1} (Found: C, 55.17; H, 6.66; S, 26.29; Ni, 12.68. $C_{22}H_{30}NiS_4$ requires C, 54.88; H, 6.28; S, 26.64; Ni, 12.21%). ESI-MS: 481 = [M + H]$^+$.

[Ni(xbsms)]. To a suspension of [Ni(acac)$_2$] (0.173 g, 0.59 mmol) in 50 ml ethanol was added one equivalent **8** (0.297 g, 0.59 mmol) and two equivalents NMe_4OH (0.214 g, 1.18 mmol). The mixture was refluxed for 1 hour, then the unreacted [Ni(acac)$_2$] was removed by filtration and the volume of the filtrate was reduced *in vacuo* to 10 ml. The dark green product was collected in a yield of 0.170 g (71%). Crystals suitable for X-ray diffraction were obtained from $CHCl_3/Et_2O$. δ_H [300.13 MHz, $CDCl_3$, 300 K] 7.28 (m, 2H, Ph–H3, Ph–H6), 7.19 (m, 2H, Ph–H4, Ph–H5), 3.83 (s, 4H, Ph–CH_2–S–), 2.22 (s, 4H, –C$(CH_3)_2$–CH_2–S–), 1.69 (s, 12H, CH_3). ν_{max}/cm^{-1} 2954m, 2887m, 2820m, 1433m, 1455s, 1362s, 1248m, 1133s, 1074s, 949m, 788s, 771s, 702s, 605m, 492s, 465s, 390m, 360s, 341s cm^{-1} (Found: C, 47.33; H, 6.13; S, 30.82. $C_{16}H_{24}NiS_4$ requires C, 47.65; H, 6.00; S, 31.80%). ESI-MS: 404 = [M + H]$^+$.

Crystal structure determinations

X-Ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (λ = 0.71073 Å) at a temperature of 150(2) K. The structures were solved with automated Patterson methods (DIRDIF97[27]) and refined with SHELXL-97[28] against F^2 of all reflections. Molecular illustration, structure checking and calculations were performed with the PLATON[29] package.

Ni(bsms)$_2$. The crystals were obtained as brown hexagons. The absorption correction was based on multiple measured reflections (program PLATON[29] routine MULABS, 0.76–0.81 transmission). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups.

Ni(xbsms). The crystals were obtained as dark red blocks. The absorption correction was based on multiple measured reflections (program PLATON[29] routine MULABS, 0.75–0.83 transmission). Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were refined as rigid groups.

CCDC reference numbers 174229 and 174230.

See http://www.rsc.org/suppdata/dt/b1/b110332f/ for crystallographic data in CIF or other electronc format.

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