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Iron and Nickel Complexes Containing β-Diketiminato Ligands with Thioether Tethers

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Dedicated to Dr. habil. Werner Hanke in Recognition and with Gratitude for his work done for this Journal over the Last Decades

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Abstract. A novel β-diketiminato ligand precursor, LH (**II**), containing thioether tethers was synthesized by the reaction of acetylacetone and 2-methylthioaniline. **II** was deprotonated and used in the synthesis of two iron(II) complexes, [LFeCl] (**1**), and [LFeOTf] (**2**), and one nickel(II) complex, [LNiBr] (**3**). All three compounds were characterized by means of single crystal X-ray diffraction and their structures are discussed.

Introduction

β-Diketiminates have proven to be very versatile ligands in the past, both in main group and transition metal chemistry [1]. They stabilize high as well as low oxidation states, and they can be used to prepare coordinatively unsaturated complexes [2]. We are interested in utilising this ligand system for the structural modelling of the dinuclear prosthetic groups of the [FeFe] and [NiFe] hydrogenases. In both of these enzymes the two metal centres are bridged by thiolate ligands and hence β-diketiminato ligands containing additional tethers with sulphur donor atoms seemed of special interest. One ligand system of that type had been reported in the literature already (see Scheme 1) [3]: In **I** the aryl rings at the imino groups are substituted by thiophenol units so that after triple deprotonation a tetradentate potential ligand results. After complexation of the first metal in its centre further coordination of a second metal at the thiolate ligands was envisaged for future research.

Experimental Section

General Procedures

All manipulations were carried out in a glove-box or else under an atmosphere of dry and oxygen-free argon with Schlenk techniques. Microanalyses were performed on a Leco CHNS 932 elemental analyser and a HEKAtech Euro EA 3000 elemental analyser. Infrared (IR) spectra were recorded in the region 4000 − 400 cm^{-1} using samples prepared as KBr pellets with a Digilab Excalibur FTS 4000 FTIR-spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AV 400 spectrometer in chloroform-*d*. The spectra were calibrated against the internal residual proton and natural abundance ^{13}C resonances of the deuterated solvent ($CDCl_3$ δ_H 7.26 ppm, δ_C 77.0 ppm). Measurements of effective magnetic moments were performed on a Alfa magnetic susceptibility balance.

Materials

Solvents were purified, dried and degassed prior to use. 2-methylthioaniline [4] and $[Fe(OTf)_2(MeCN)_2]$ [5] were prepared according to the literature procedure. $[NiBr_2dme]$ was prepared by stirring $NiBr_2$ in boiling dme for 48 hours, followed by filtration and drying in vacuum.

Synthesis

II: 4.20 g 2,4-pentadione (0.04 mol), 12.15 g 2-methylthioaniline (0.09 mol) and 7.23 g *p*-toluenesulfonic acid monohydrate (0.04 mol) were heated in 100 mL of toluene to reflux for 48 h, while any water generated was removed by a Dean-Stark trap. Subsequently, the solvent was removed in vacuum, and the yellow-brown residue was extracted with 100 mL of CH_2Cl_2. The yellow solution was washed three times with a saturated aqueous $NaHCO_3$ solution, and the aqueous phase extracted three times with CH_2Cl_2. The unified organic phases were dried over $MgSO_4$ and the solvent was removed under vacuum. After recrystallisation from MeOH (twice) 7.815 g (0.02 mol, 52 %) of pure **II** were obtained in form of a yellow solid. Melting point 103-105 °C. Elemental analysis for $C_{19}H_{22}N_2S_2$ (342.52 $gmol^{-1}$); C 66.58 (calc. 66.62); H 6.77 (6.47); N 8.12 (8.18) %.

^{1}H-NMR ($CDCl_3$): δ = 12.49 (s, 1H, N-*H*), 7.17 (m, 2H, Ar-*H*), 7.09 (m, 4H, Ar-*H*), 6.95 (m, 2H, Ar-*H*), 4.96 (s, 1H, N=C-C*H*), 2.37 (s, 6H, S-CH_3), 1.92 (s, 6H, N=C-CH_3). **^{13}C-NMR** $\{^{1}H\}$ ($CDCl_3$): δ = 160.0 (N=*C*), 142.7 (N-*C*), 132.6, 124.8, 124.3, 123.9, 123.0 (Ar-*C*), 96.3 (N=C-*C*H′), 20.1 (N=C-*C*H_3), 14.5 (N=C-*C*H_3). **IR** (KBr) /cm^{-1}: 3053 w, 2918 w, 1619 vs,

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1581 s, 1530 vs, 1496 vs, 1459 vs, 1436 vs, 1425 vs, 1378 s, 1362 s, 1348 s, 1318 m, 1278 vs, 1266 vs, 1187 vs, 1164 m, 1127 m, 1070 s, 1039 s, 1026 s, 965 w, 951 w, 924 m, 855 w, 801 w, 774 w, 755 vs, 737 s, 697 m, 680 m, 638 w, 597 w, 560 w, 541 w, 455 w, 440 w, 415 w.

[LFeCl] (1): 2.5 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane (0.004 mol) were added to a yellow solution of 1.370 g **II** (0.004 mol) in 10 mL of thf cooled to −78 °C. After annealing to r.t. the yellow solution was added slowly (within 20 min.) to a suspension of 0.507 g (0.004 mol) $FeCl_2$ in thf. After stirring for 2 h the solvent was removed under vacuum and the resulting red residue was washed with 5 mL of *n*-hexane. Afterwards it was extracted with *n*-hexane/CH_2Cl_2 (1:10), and filtering followed by removal of the volatiles yielded 0.710 g of crude **1**. After recrystallisation from *n*-hexane/thf (1:10) 0.620 g (0.002 mol, 36 %) of pure **1** was obtained in form of red crystals. Elemental analysis for $C_{19}H_{21}ClFeN_2S_2$ (432.81 gmol^{-1}); C 52.58 (calc. 52.73); H 5.11 (4.89); N 6.44 (6.47); Cl 8.69 (8.19) %.

Single crystals could be obtained by cooling a concentrated diethylether solution to 4 °C for 2 days.

IR (KBr) /cm^{-1}: 3057 w, 2965 w, 2923 w, 1533 s, 1458 vs, 1428 s, 1371 vs, 1358 vs, 1283 s, 1195 m, 1130 w, 1097 w, 1067 w, 1027 m, 939 m, 864 w, 804 w, 782 w, 753 s, 739 m, 711 w, 656 w, 629 w, 551 w, 491 w, 466 w, 419 w, 327 m, 302 w. μ_{eff} = 4.95 B.M. (29 °C).

[LFeOTf] (2): 0,53 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane (0.80 mmol) were added to a yellow solution of 274 mg **II** (0.80 mmol) in 10 mL thf cooled to −78 °C. After annealing to r.t. the yellow solution was added slowly (within 20 min.) to a colourless solution of 349 mg [Fe(OTf)$_2$(MeCN)$_2$] (0.80 mmol) in thf. After stirring for 2 h the solvent was removed under vacuum, and the resulting red residue washed with 5 mL of *n*-hexane. Afterwards it was extracted three times with 7 mL diethylether, and after concentration and cooling 80 mg (0.15 mmol, 18 %) of **2** were obtained in form of red crystals. Elemental analysis for $C_{20}H_{21}F_3FeN_2O_3S_3$ (546.43 gmol^{-1}); C 43.77 (calc. 43.96); H 4.04 (3.87); N 4.99 (5.13) %.

Single crystals could be obtained bei cooling a concentrated diethylether solution to 4 °C for 2 days.

IR (KBr) /cm^{-1}: 3052 w, 2979 w, 2917 w, 1637 w, 1578 w, 1521 m, 1458 s, 1436 s, 1381 vs, 1315 s, 1278 vs, 1262 s, 1239 s, 1186 s, 1127 w, 1029 s, 972 w, 865 w, 828 w, 754 m, 734 m, 636 m, 516 w, 454 w, 425 w.

[LNiBr] (3): 2.5 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane (0.004 mol) were added to a yellow solution of 1.370 g **II** (0.004 mol) in 10 mL of thf cooled to −78 °C. After annealing to r.t. the yellow solution was added slowly (within 20 min.) to a suspension of 1.235 g [NiBr$_2$dme] (0.004 mol) in thf. After stirring for 2 h the solvent was removed under vacuum, and the resulting brown-green residue washed with 10 mL of Et_2O. Afterwards it was dissolved with 10 ml CH_2Cl_2 and after concentration followed by cooling (4 °C) 0.820 g (0.002 mol, 40 %) of pure **3** were obtained in form of dark green crystals suitable for X-ray diffraction analysis. Elemental analysis for $C_{19}H_{21}BrN_2NiS_2$ (480.11 gmol^{-1}); C 47.19 (calc. 47.53); H 4.87 (4.41); N 5.48 (5.83); Br 16.88 (16.64) %.

IR (KBr) /cm^{-1}: 3058 w, 2988 w, 2965 w, 2918 w, 1523 s, 1449 vs, 1434 vs, 1413 s, 1361 vs, 1308 s, 1281 vs, 1267 vs, 1230 s, 1192 s, 1157 s, 1128 m, 1065 m, 1033 s, 1020 s, 968 m, 957 w, 942 m, 861 w, 833 w, 779 w, 772 m, 752 s, 742 s, 729 s, 698 m, 667 w, 659 w, 631 w, 561 w, 549 w, 523 w, 490 w, 473 w, 458 w, 422 w, 396 w, 355 w, 328 w, 309 w, 268 w. μ_{eff} = 2.73 B.M (24 °C).

Crystal Structure Determinations

The data of **1**, **2** and **3** were collected on a Stoe IPDS 2T diffractometer using $Mo_{K\alpha}$ radiation, λ = 0.71073 Å. In all cases, the structures were solved by direct methods (SHELXS-97) [6] and refined versus F^2 (SHELXL-97) [7] with anisotropic temperature factors for all non-hydrogen atoms (Table 1). All hydrogen atoms were added geometrically and refined by using a riding model. Unfortunately in the case of **3** the low quality of the crystals obtained did not allow for better values R_1 and wR_2 and resulted in residual electron density in the final Fourier map.

Table 1. Crystal data and experimental parameters for the crystal structure analyses for **1**, **2** and **3**.

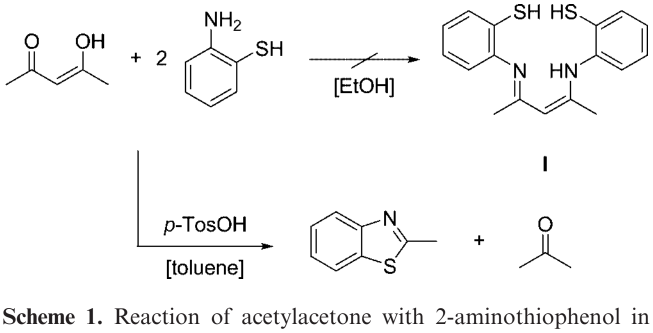
	1·1/2 OEt_2	**2**	**3**
molecular formula	$C_{42}H_{52}Cl_2Fe_2N_4OS_4$	$C_{20}H_{21}F_3FeN_2O_3S_3$	$C_{19}H_{21}BrN_2NiS_2$
formular weight /g·mol^{-1}	939.72	546.43	480.11
temperature /K	150(2)	150(2)	210(2)
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	P-1	$P2_1/n$
a /Å	15.260(2)	10.6840(6)	15.265(2)
b /Å	6.6058(5)	11.1039(6)	6.6423(5)
c /Å	21.608(3)	23.912(2)	21.790(3)
α /deg		100.560(4)	
β /deg	94.934(11)	93.250(4)	94.272(11)
γ /deg		118.214(4)	
V /Å^3	2170.1(4)	2423.5(3)	2203.2(5)
Z	2	4	4
densitiy /g·cm^{-3}	1.438	1.498	1.447
μ(MoK_α) /mm^{-1}	1.022	0.928	2.888
F(000)	980	1120	976
GooF	1.163	1.101	1.173
R_1 [I>2σ(I)]	0.0799	0.0374	0.1183
wR_2 (all data)	0.1939	0.0855	0.3145
Δρmax / Δρmin /e·Å^{-3}	0.810 / −0.747	0.818 / −0.518	1.922 / −1.322

Crystallographic data for the structures of **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 697485 (**1**), 697484 (**2**), 697486 (**3**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Syntheses of Mononuclear Fe and Ni Complexes Containing L

Trying to reproduce the synthesis reported for **I** [3] it was found that the reaction of acetylacetone with 2-aminothiophenol in ethanol does not lead to the red crystalline solid described which had been identified as **I** by means of NMR-spectroscopy and elemental analysis (Scheme 1). In contrast to the literature statements the two compounds

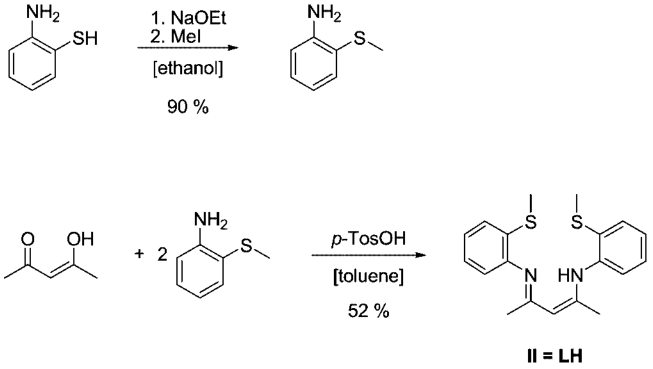


Scheme 1. Reaction of acetylacetone with 2-aminothiophenol in toluene does not lead to the β-diketimine **I**.

failed to react in boiling ethanol, and therefore more forcing conditions were applied: The conversion was performed in toluene in the presence of catalytic amounts of *p*-TsOH under heating (employing a Dean-Stark trap). After distillation a colourless oil was obtained. Its elemental analysis was in accordance with the data calculated for **I**. However, extensive one- and two-dimensional NMR spectroscopic measurements identified the product as 2-methylbenzothiazole.

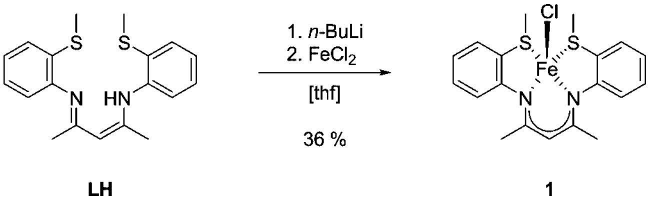
As formation of 2-methylbenzothiazole proceeds via attack of the thiol units at the acetylacetone carbonyl units [8], we decided to replace these by thioether functions. Hence, 2-aminothiophenol was alkylated with methyliodide [4] and reaction of the resulting 2-methylthioaniline with acetylacetone under acid catalysis by *p*-TsOH in toluene yielded the desired ligand precursor **II** in 52 % yield (Scheme 2).

After deprotonation of **II** with *n*-BuLi at −78 °C in thf the resulting lithium salt LiL can be reacted in-situ with metal halides to obtain the corresponding metal complexes. Care has to be taken, however, that the metal precursor is never surrounded by excessive L^-, since otherwise homoleptic complexes ML_2 are formed. We have made this experience in one instance where subsequently crystals of FeL_2 were isolated. Although the solution of an X-ray crystal structure analysis did not reach a quality that would allow a detailed discussion of bond lengths and angles, it revealed that the Fe atom is coordinated tetrahedrally by the four N donor functions of two ligand equivalents, while the thioether functions do not interact. As the metal centre is effectively shielded by L_2, any further reactivity is precluded, so that such complexes are not suitable for our future plans. We have therefore not pursued further characterisation.



Scheme 2. Synthesis of the ligand precursor **II**.

Bearing this problem in mind, a solution of LiL in thf was dropped slowly to a suspension of $FeCl_2$ in thf in order to obtain the iron complex [LFeCl], **1**, (Scheme 3).



Scheme 3. Synthesis of the iron complex [LFeCl] (**1**).

After appropriate work-up **1** was characterised by elemental analysis, IR spectroscopy as well as by single crystal X-ray diffraction. The molecular structure is depicted in Figure 1. The iron centre is located in a distorted square pyramidal coordination sphere that is formed by the two N donor atoms and the thioether functions (which represent the basis) as well as one chloride ligand. As expected, the Fe-N bonds in **1** (2.057(6) and 2.055(6) Å) are somewhat longer than those observed in comparable unfunctionalised, tetracoordinated diketiminato iron complexes (from 1.978(1) to 2.002(1) Å, [9]), as the thioether donor functions pull the iron centre slightly out of the diiminato binding pocket and generally bond lengths increase with increasing coordination numbers.

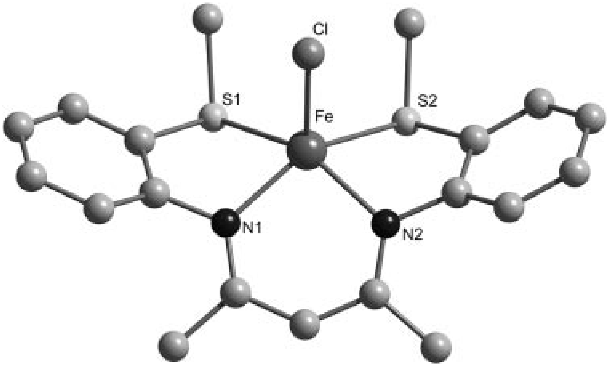
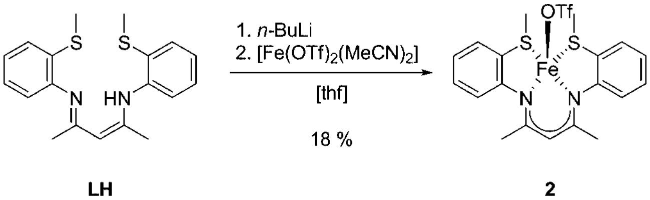


Figure 1. Molecular structure of **1**. All hydrogen atoms were omitted for clarity.

Selected bond lengths /Å and angles /°: Fe-Cl 2.258(2), Fe-N1 2.057(6), Fe-N2 2.055(6), Fe-S1 2.507(2), Fe-S2 2.526(2), Cl-Fe-N1 113.3(3), Cl-Fe-N2 111.2 (2), Cl-Fe-S1 104.05(7), Cl-Fe-S2 103.26(8), N1-Fe-N2 91.7(2), N1-Fe-S1 78.5(3), N1-Fe-S2 143.4(3), N2-Fe-S1 144.4(2), N2-Fe-S2 77.4(2), S1-Fe-S2 90.24(7).

The Fe−S bond lengths of **1** (2.507(2) and 2.526(2) Å) are significantly longer than those of the only pentacoordinated iron(II) complex with thioether ligands described in the literature (2.2250 to 2.2303 Å, [10]), which hints to a weaker interaction between the iron and the sulphur atoms in **1**. The effective magnetic moment of **1** measured for the solid at r.t. amounts to 4.95 μ_B which indicates a high-spin configuration at the iron(II) ion. **1** is very sensitive to air: even traces of O_2 lead to an immediate colour change of a thf solution from red to dark brown. This is understandable as **1** contains a coordinatively unsaturated Fe^{II} atom that is readily accessed by O_2.

Adding a thf solution of LiL slowly to a thf solution of $[Fe(OTf)_2(MeCN)_2]$ allows the isolation of a corresponding triflate complex [LFeOTf] (**2**), (Scheme 4) in moderate yields, which however dimerises via the triflate ligands in the solid state, as revealed by a single crystal X-ray diffraction study (see Figure 2): two LFe cores are bridged by two O−S=O units as part of the triflate ions. For **1** such a



LH **2**

Scheme 4. Synthesis of the iron complex [LFeOTf] (**2**).

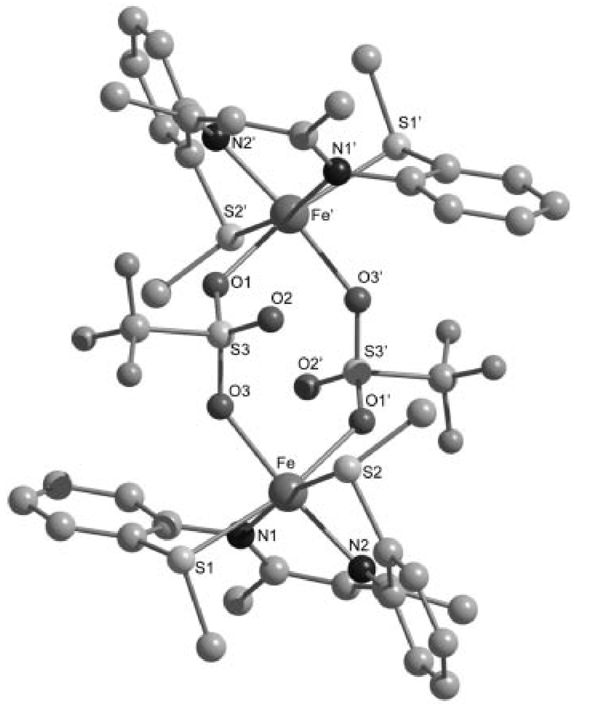
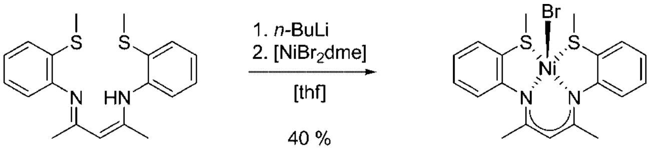


Figure 2. Molecular structure of **2**. All hydrogen atoms were omitted for clarity.

Selected bond lengths /Å and angles /°: Fe-N1 2.074(2), Fe-N2 2.039(2), Fe-S1 2.6028(9), Fe-S2 2.5073(8), Fe-O3 2.096(2), S3-O1 1.438(2), S3-O2 1.422(2), S3-O3 1.453(2) Fe-Fe′ 5.5098(7), Fe′-O1 2.200(2), Fe-O1′ 2.096(2),Fe′-O3′ 2.200(2), S3′-O1′ 1.438(2), S3′-O3′ 1.453(2), N1-Fe-N2 88.79(9), N1-Fe-O3 96.30(9), N1-Fe-S1 76.67(7), N1-Fe-S2 167.02(7), N2-Fe-O3 174.08(9), N2-Fe-S1 101.48(7), N2-Fe-S2 81.80(6), S1-Fe-S2 96.38(3), S1-Fe-O3 82.71(6), S2-Fe-O3 93.63(6), O3-S3-O1 112.6(2), O3-S3-O2 115.2(2), O1-S3-O2 116.3(2).

dimerisation is not possible as a mononuclear bridge would certainly lead to repulsions between the two LFe cores. The Fe-O and S-O bond distances are significantly different (S3-O3: 1.453(2) Å vs. S3-O1:1.438(2) Å; Fe-O3: 2.096(2) Å vs. Fe′-O1: 2.200(2) Å), which hints to Fe-O-S=O···Fe units with localised charges and π bonds. The Fe-N and Fe-S bonds within **2** are comparable to those found in **1**, even though − unlike in **1** − the N and S donor atoms are not at all located in a plane. Accordingly, the iron centres in **2** show distorted octahedral coordination spheres. Nevertheless, **2** is very sensitive to air, too, probably due to a facile replacement of the weakly coordinating OTf ligands.

For the preparation of a nickel complex the binary nickel halides cannot be employed as their solubilities in organic solvents are very low so that the formation of homoleptic L_2Ni complexes will predominate. Thus, the more soluble [NiBr$_2$dme] was dissolved in thf and treated with LiL. Appropriate work-up led to dark green crystals of [LNiBr], **3**, (Scheme 3) and the result of an X-ray structure determination is shown in Figure 3.



LH **3**

Scheme 5. Synthesis of the nickel complex [LNiBr] (**3**).

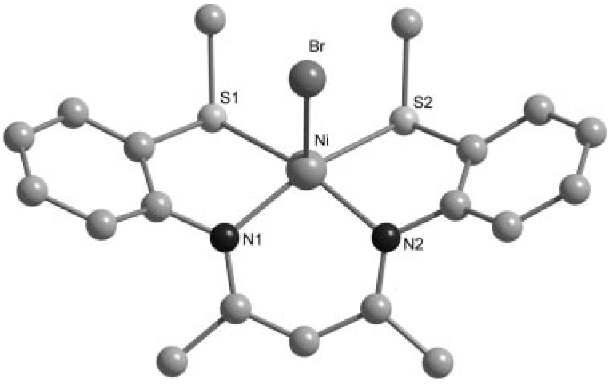


Figure 3. Molecular structure of **3**. All hydrogen atoms were omitted for clarity.

Selected bond lengths /Å and angles /°: Ni-Br 2.404(2), Ni-N1 2.01(1), Ni-N2 1.98(2), Ni-S1 2.411(4), Ni-S2 2.424(4); Br-Ni-N1 105.1(4), Br-Ni-N2 103.8(4), Br-Ni-S1 98.6(2), Br-Ni-S2 98.5(2), N1-Ni-N2 95.5(5), N1-Ni-S1 81.5(4), N1-Ni-S2 156.4(4), N2-Ni-S1 157.4(4), N2-Ni-S2 80.8(4), S1-Ni-S2 93.0(2).

The structure of the LNi core of **3** is similar to the one of the LFe core in **1**; however, due to the slightly smaller ionic radius of Ni^{2+} in comparison to Fe^{2+} the bond distances in **3** are somewhat shorter. An analogous bond shortening has been observed before comparing unfunctionalised β-diketiminato iron and nickel complexes [11]. Compared to other pentacoordinate nickel(II) complexes with thioether ligands described in the literature, the Ni-S bond lengths in **3** (2.411(4) and 2.424(4) Å) are clearly in the range of weaker Ni-thioether bonds (2.377(4) to 2.5597(10) Å) [12]. The effective magnetic moment measured for the solid at r.t. amounts to 2.73 μB which is indicative of a high-spin configuration at the nickel(II) ion.

Future research will now focus on utilising compounds **1**−**3** as synthons for the preparation of heterobimetallic Fe/Ni compounds as models for [NiFe] hydrogenases.

Conclusions

We have synthesized a novel β-diketimine functionalized by thioether tethers, LH, **II**, which, after deprotonation, can easily be used as a tetradentate ligand. One nickel(II) and two iron(II) complexes have been synthesised via the reaction of the lithiated ligand LLi with the appropriate metal salts and were fully characterized. The halide complexes [LFeCl] (**1**), and [LNiBr] (**3**), adopt similar structures with the metal ions in a square pyramidal coordination environment. In these compounds the square plane is formed by the ligand while the apical position is occupied by the halide atom. A different situation can be observed in the corresponding iron(II) triflate complex [LFeOTf] (**2**): In the solid phase **2** forms a dimer with O−S=O-units of the triflate ions in the bridging positions. In consequence the ligand in **2** adopts a distorted conformation so that the iron atoms are located in a distorted octahedral coordination sphere. Magnetic measurements revealed that the metal centers in the complexes **1** and **3** adopt a high spin configuration, that is, the ligand field caused by the ligand L^- is − as in case of other diketiminates − not very strong.

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