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Nickel(II) tri-*tert*-butoxysilanethiolates with N-heterocyclic bases as additional ligands. Synthesis, molecular structure and spectral studies.

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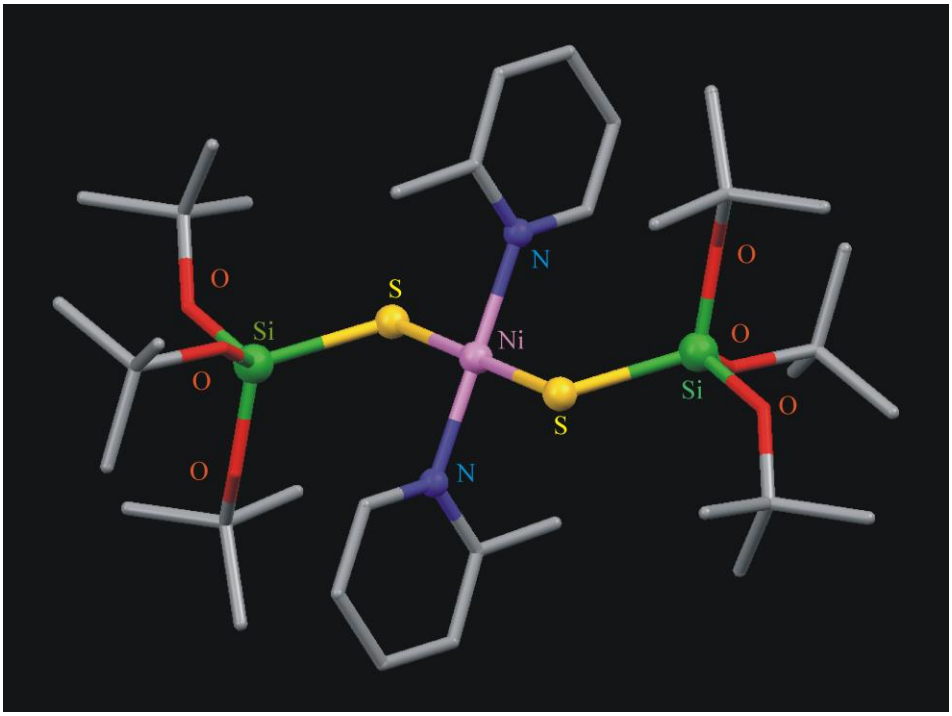
Abstract

Three heteroleptic, neutral nickel(II) tri-*tert*-butoxysilanethiolates with monodentate heterocyclic bases - pyridine, 2-methylpyridine and 3,5-dimethylpyridine respectively, serving as additional ligands have been prepared following the same synthetic procedure. Complexes were characterized by single crystal X-ray structure determination and elemental analysis. For complexes **1** and **2** FT-IR and UV-vis spectroscopy have been additionally followed.

Three different coordination motifs have been observed. Molecules building tetragonal crystals of $[Ni\{SSi(O^tBu)_3\}_2(C_5H_5N)]$ **1** feature Ni(II) coordinated by two S,O-chelating tri-*tert*-butoxysilanethiolato residues and one N atom of pyridine in a strongly distorted trigonal bipyramidal environment. Complex $[Ni\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ **2** forms triclinic crystals and its core atoms adopt a planar geometry with Ni(II) in the middle of the N_2S_2 plane. Molecules of complex $[Ni\{SSi(O^tBu)_3\}_2(C_7H_9N)_2(H_2O)]$ **3** form orthorhombic crystals with penta-coordinated Ni(II) in a distorted tetragonal pyramidal $NiN2OS_2$ environment.

Complex **2** roughly mimics one of two metal centers in active site of ACS/CODH enzyme.



Keywords: Nickel(II); Tri-*tert*-butoxysilanethiolate; Crystal structure; N ligand; Spectroscopic study

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1. Introduction

Nickel complexes with thiolate or sulfido coordination sphere have been intensively studied for their applications. Monolayered nickel alkanethiolates for instance show antiferromagnetic coupling [1, 2], while planar tetracoordinated low-spin nickel(II) thiolates oxidize with the conversion to S-bonded sulfinato complexes by incorporation of dioxygen [3].

Nickel plays various roles in biological systems. At least eight nickel-dependent enzymes that represent a wide range of interesting chemistry have been identified and characterized. Amidst them is carbon monoxide dehydrogenase (CODH) [4] which interconverts CO and CO_2 and acetyl-coenzyme A synthase/carbon monooxide dehydrogenase (ACS/CODH) [5], that converts CO gas into a carbon source. NiFe hydrogenase catalyzes the reversible oxidation of hydrogen gas [6].

Nickel proteins present diverse types of coordination modes on metal ion, however the general insight into four nickel-binding sites that have been so far identified in enzymatic structures shows the tendency of adopting a square-planar geometry on metal ion [7]. For instance, nickel superoxide dismutase (NiSOD) in the fully reduced form contains Ni(II) with square planar geometry. The oxidation state changes to Ni(III) and spatial arrangement around the metal ion to square pyramidal when the enzyme is in resting state [8]. The transcription factor NikR, which plays a role of cytoplasmic nickel sensor in *Escherichia coli* and *Helicobacter pylori* is build of four units and each of them contains Ni(II) in a square-planar coordination environment consisting of two histidines and one cysteine from one NikR subunit and another histidine from the adjacent subunit. The structure of the whole molecule of this protein in *apo* form suggests that the role of nickel is crucial for proper conformation and activity of the protein [9].

Large part of studies devoted to nickel proteins is dedicated to analysis of the structure of A-cluster active site of ACS/CODH enzyme. This particular protein attracts attention because of its significance role in the global carbon cycle. The active site of A-cluster of ACS/CODH consists of Fe_4S_4 cubane bridged by a cysteine thiolate to a dinuclear M(μ-S)M' cluster where M is nickel and M' may be Ni(II), Zn(II) or Cu(I). The coordination on nickel center is completed by two backbone carboxamido nitrogen atoms resulting in a NiN_2S_2 square-planar arrangement [5].

In recent years, our work has been targeted towards biomimetic studies and the prevalent part of these was devoted to zinc thiolates [10]. Now we turn our attention to nickel complexes with S-thiolate and N-donor ligands that may serve as biomimetic models of active sites of nickel-containing proteins.

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The synthesis of transition metal complexes with thiolate ligands presents some difficulties because of strong bridging tendency of thiolate sulfur leading to the formation of oligo- and polymeric species [11]. One of the strategies which help to avoid such undesirable side process is the use of sterically hindered thiolate ligands.

For many years we have been studying the chemistry of silanethiols as a special type of thiols. Our research group showed that tri-*tert*-butoxysilanethiol used as a source of very bulky thiolate ligand clearly reduces the tendency of sulfur promoted polymerization and allowed us to obtain numerous mono- and binuclear heteroleptic silanethiolate complexes [12-24]. Moreover, unlike many others, this particular silanethiol is resistant towards hydrolysis and syntheses may be followed in atmospheric conditions [25]. We have obtained and structurally characterized not only stable tri-*tert*-butoxysilanethiolates of divalent cobalt, zinc and cadmium, but also those of manganese(II) and recently iron(II) [18, 24]. In some of them the immediate environment on metal center follows that found in active site of alcohol dehydrogenase (ADH) [23, 24a] and one of them $[Zn\{SSi(O^tBu)_3\}_2(C_7H_9NO)]$ was tested for the catalytic properties [26]. We have also affirmed that some heteroleptic cobalt(II) tri-*tert*-butoxysilanethiolates are isomorphous to related zinc(II) complexes and can be considered as spectral models of ADH protein in solution [22].

So far the majority of nickel(II) thiolates serving as structural mimics of the active sites of NiSOD, NikR and ACS/CODH enzymes employed N, S ligands of chelating type [27]. Only few examples of Ni(II) complexes with monodentate N- and S-ligands are known [28]. For those reasons we directed our investigations towards heteroleptic nickel(II) thiolates with the use of monodentate N-donor ligands. Our previous results prompted us to attempt the synthesis of complexes with NiN_2S_2 core related to the coordination mode present in ACS/CODH protein. In this paper we report synthesis, structural and spectroscopic characterization of three heteroleptic tri-*tert*-butoxysilanethiolate complexes of Ni(II) bearing additional pyridine related ligands of different steric hindrance and different basicity. The synthetic strategy presented here has led to complexes with three different coordination geometries: trigonal bipyramidal in **1**, square-planar in **2**, and tetragonal pyramidal in **3** (Scheme 1).

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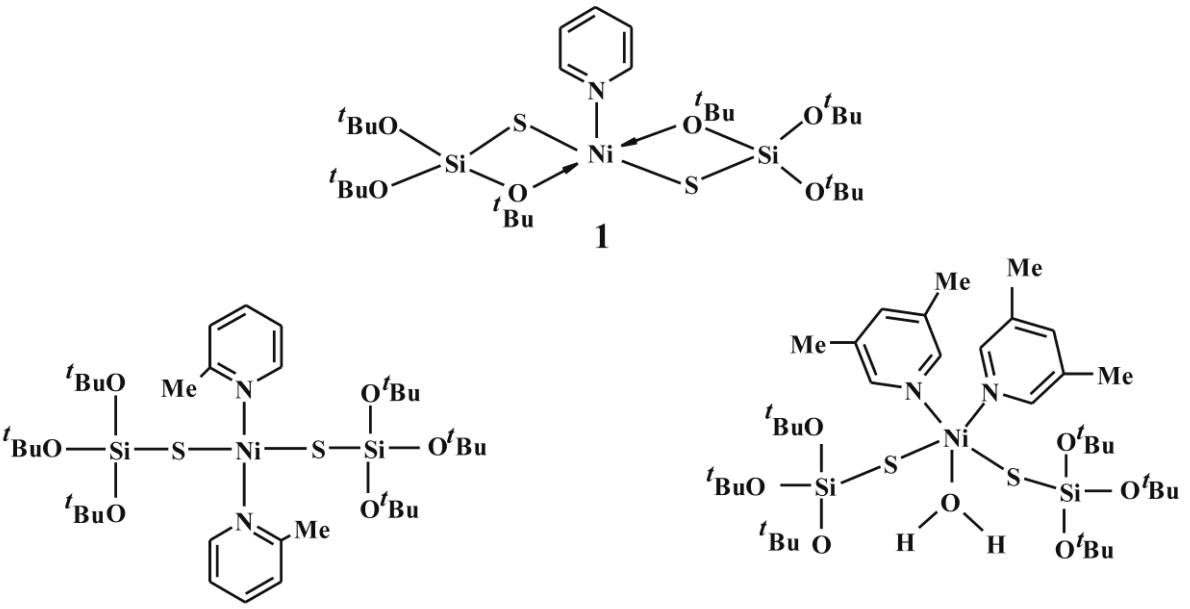

Scheme 1. Obtained complexes **1 - 3**.

2. Results and Discussion

2.1 Synthesis

All three complexes $[Ni\{SSi(O^tBu)_3\}_2(C_5H_5N)]$ **1**, $[Ni\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ **2** and $[Ni\{SSi(O^tBu)_3\}_2(C_7H_9N)_2(H_2O)]\cdot(C_6H_6)$ **3** were obtained following the same synthetic procedure. To a solution of $NiCl_2$ in water respective heterocyclic base was added followed by addition of silanethiol. The reagents were taken in a 1 : 4 : 2 molar ratio with the base serving as ligand and HCl acceptor. Water insoluble products were collected and recrystallized from organic solvents. Complexes **1** and **2** are stable and can be stored in atmospheric conditions for months, in contrast to unstable complex **3**. The bases used for syntheses were chosen because of their different basicities (pK_a: pyridine 5.20, 2-methylpyridine 5.90, 3,5-dimethylpyridine 6.15) and spatial requirements.

The reaction with pyridine leads to compound **1**. Its composition was initially established with the use of elemental analysis which pointed to the 1:2 molar ratio of nitrogen and sulfur and thus two silanethiolate residues and one pyridine molecule coordinated to the metal ion. Also FT-IR solid state spectrum of **1** showed the presence of frequencies typical for heterocyclic base and Si–O–C bonding from silanethiolate residue. The composition and structure of the complex was finally established with the use of X-ray analysis showing metal ion coordinated

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by one molecule of pyridine and two O, S-chelating silanethiolato residues in a $NiNO_2S_2$ type of arrangement. Such type of complexes were synthesized previously for Co(II) and Zn(II) [12, 13, 15, 16].

The exchange of pyridine for more basic and more sterically hindered 2-methylpyridine gave another product with a formula $[Ni\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ **2.** Again, its composition and structure was established by elemental analysis, FT-IR spectroscopy and X-ray of single crystal. Surprisingly, unlike **1**, we found in **2** two N-donor ligands within Ni(II) coordination sphere. This was accompanied by a change of bonding mode of both tri-*tert*-butoxysilanethiolato ligands from chelating as in **1** to strictly monodentate in **2** and thus formation of NiN_2S_2 central core. Syntheses performed previously for Co(II) and Zn(II) tri-*tert*-butoxysilanethiolates with the same pyridine derivative resulted among others in a penta-coordinated $[M\{SSi(O^tBu)_3\}_2(C_6H_7N)]$ [12, 23].

Finally, we used 3,5-dimethylpirydine and following the same synthetic procedure once more obtained another type of product - deep violet crystals of complex $[Ni\{SSi(O^tBu)_3\}_2(C_7H_9N)_2(H_2O)(C_6H_6)]$ **3**. Its structure was solved by X-ray revealing Ni(II) coordinated by two monodentate silanethiolato residues, two N-donor bases and one water molecule with the central core adopting NiN_2OS_2 form. We have noticed that at room temperature in a short period of time crystals become opaque, what may be caused by the evaporation of solvent from this sample or it may suggests the degradation of the complex. Heteroleptic tri-*tert*-butoxysilanethiolates of Co(II) and Zn(II) with 3,5-dimethylpyridine as additional ligand have been prepared by us previously [12, 19, 20] but in both cases they had $[M\{SSi(O^tBu)_3\}_2(C_7H_9N)]$ formula and chelating tri-*tert*-butoxysilanethiolato ligands, thus they resembled **1** much more then **3**.

2.2 Crystal and molecular structure determination

The molecular structures of complexes **1 - 3** with atom labeling schemes and their crystal packing are illustrated in Figs. 1- 4 and 1S-3S (Supplementary data). Selected bonds and angles are listed in Table 2.

In order to estimate the geometric shape of obtained complexes, the Addison angular structural parameter (τ) has been calculated [30, 31]. For four and five-coordinate complexes the parameters τ_4 and τ_5 respectively are defined as $\tau_4 = [360° – (\alpha – \beta)]/141°$ and $\tau_5 = (\alpha – \beta)/60°$, where α and β are the largest bond angles in the complex. For complexes with coordination number CN = 5, τ_5 becomes unity for a perfectly trigonal bipyramidal geometry

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and τ_5 = 0 for tetragonal pyramid [30]. For four coordinated complexes perfectly square planar geometry leads to τ_4 = 0 and tetrahedral geometry to τ_4 = 1 [31].

Crystals of complex **1** consist of eight molecules in a unit cell (Figs. 1 and 1S). The central Ni(II) atom is penta-coordinated by two S atoms and two O atoms derived from two O, S-chelating silanethiolate residues and one N atom of pyridine. The parameter τ_5 calculated for complex **1** has a value of 0.55 and thus its geometry is unequivocal being about halfway between a square pyramidal and a trigonal bipyramidal, albeit is slightly closer to the latter, with oxygen atoms occupying apical positions. The Ni1–O3 and Ni1–O6 distances (2.239(9) and 2.269(9) Å, respectively) clearly exceed the sum of covalent radii for Ni and O, which is equal to 1.90 Å, but are nonetheless shorter than those found in similar transition metal silanethiolates where $(^t\mathrm{BuO})_3\mathrm{SiS}$ residue behaves like bidentate ligand [12, 16, 19-21].

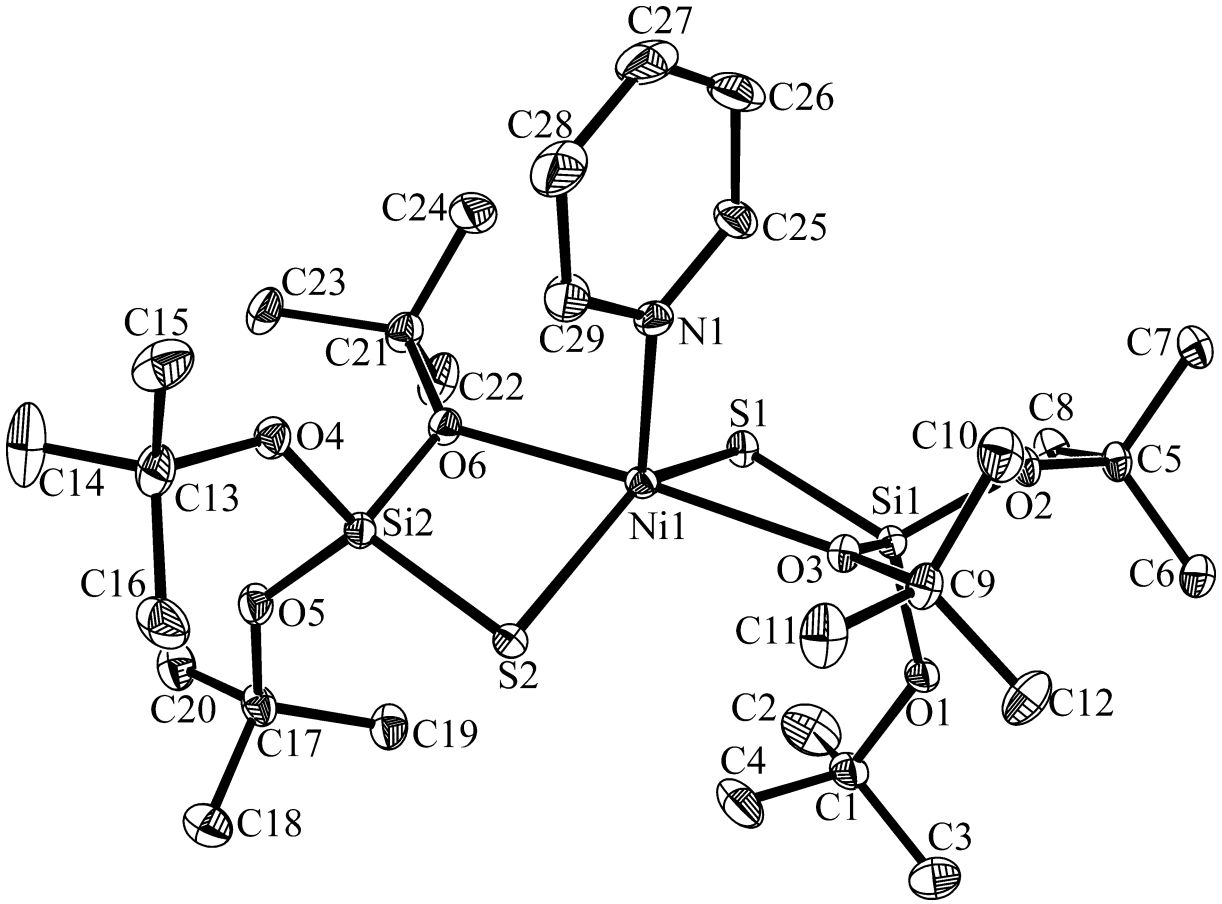

Fig 1. Molecular structure of $[Ni\{SSi(O^tBu)_3\}_2(C_5H_5N)]$ **1** with atom labeling scheme (hydrogen atoms of ^{t}BuO groups omitted, thermal ellipsoids drawn at 30% probability).

Complex **2** crystallizes with one molecule in a unit cell (Fig. 2 and 2S). Although the geometry of its NiN_2S_2 core may be approximated as square-planar (τ_4 = 0) with S1–Ni1–S2 and N1–Ni1–N2 angles being ideal 180°, the two N–Ni–S angles differ of *ca.* 10°. The Ni–S

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bond distance of 2.253(2) Å in **2** is slightly longer than those found in square-planar NiN_2S_2 complexes with scorpionate-type N_2S_2 ligands [5].

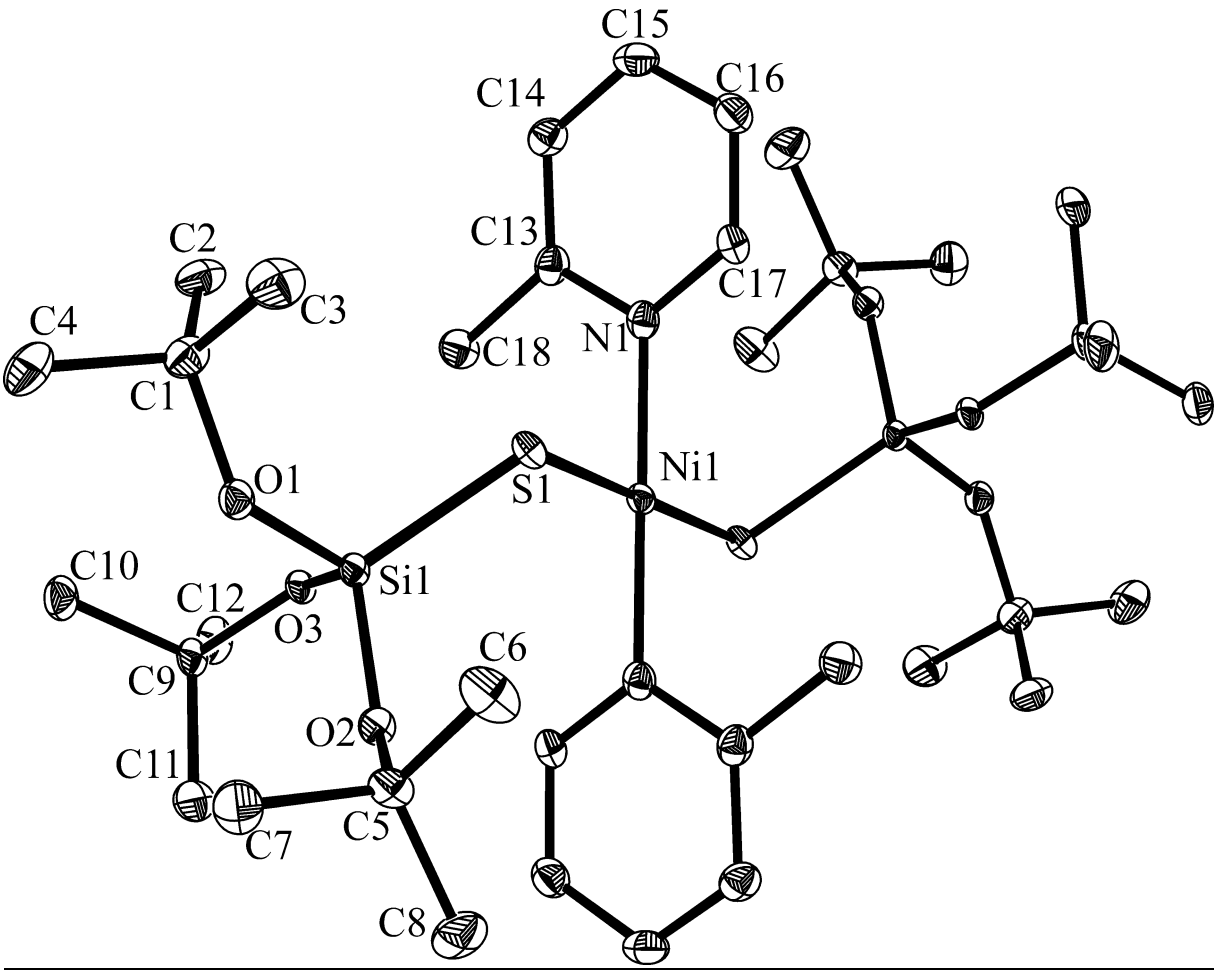

Fig 2. Molecular structure of $[Ni\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ **2** with atom labeling scheme (^{t}Bu groups and hydrogen atoms of aromatic ring omitted for clarity, thermal ellipsoids drawn at 30% probability).

Complex **3** crystallizes with eight molecules in a unit cell (Fig. 3 and 3S). Nickel coordination sphere contains five independent ligands – two silanethiolate residues, two molecules of 3,5-dimethylpyridine and one molecule of water form NiN_2OS_2 kernel. The Addison parameter τ_5 presents a value of 0.18. Hence, the geometry is a definitely closer to a square pyramidal than to a trigonal bipyramidal, but anyway it is far from the perfect one. The base of the pyramid is formed by two S atoms, O atom from water and N atom from one of the 3,5-dimethylpyridines, while the second N-base molecule forms the peak of the pyramid (Fig. 4). Nickel atom deviates of 0.301 Å from the basis plane. Bond lengths found in complex **3** are

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similar to those found in complex **1** and other penta-coordinated nickel thiolate complexes [29]. Coordinated molecule of water is engaged in the formation of two intramolecular hydrogen bonds O–H···O to oxygen atoms from adjacent *tert*-butoxy groups (Table 3). These should help to keep water in place and to provide some structural stabilization, although the effect does not seem to be a strong one, as evidenced by the lability of the compound.

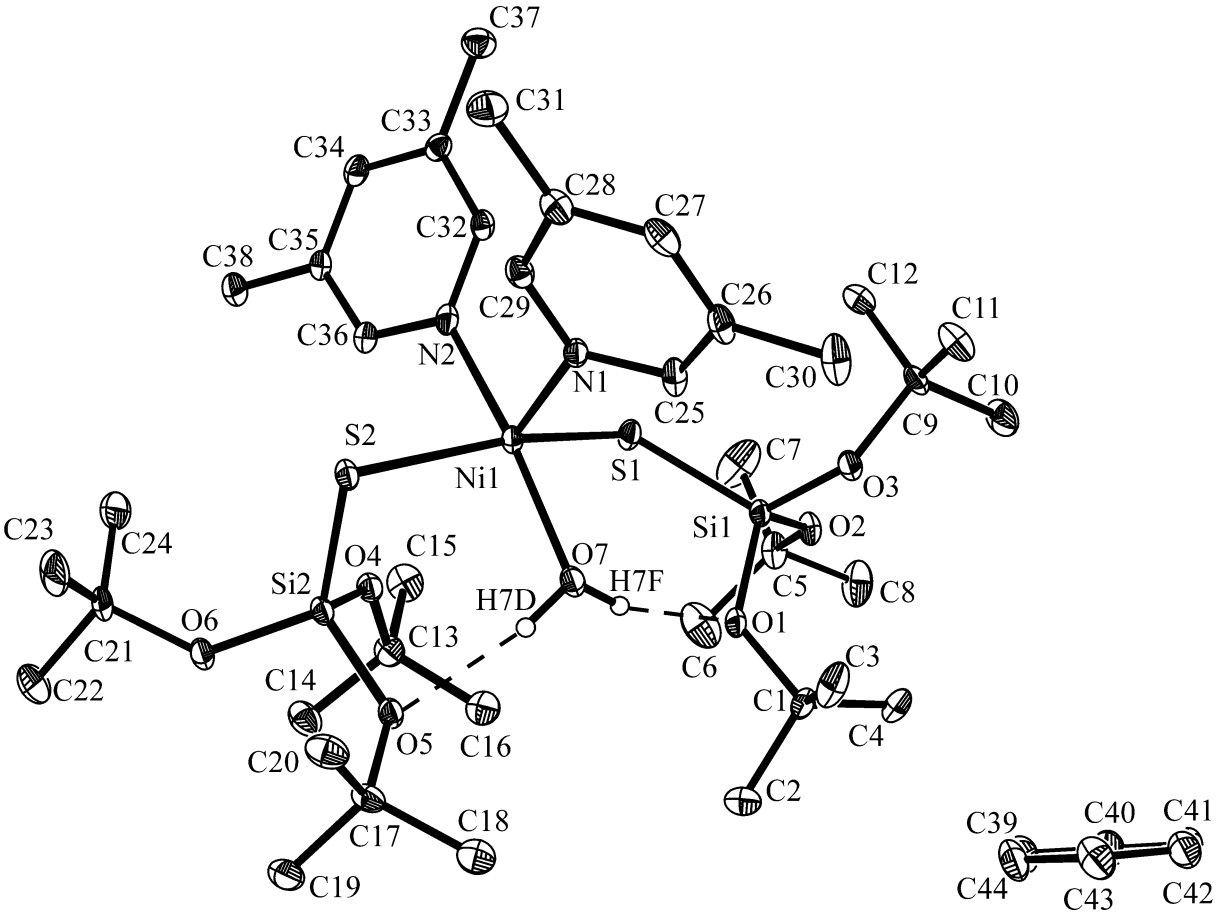

Fig 3. Molecular structure of $[Ni\{SSi(O^tBu)_3\}_2(C_7H_9N)_2(H_2O)]\cdot C_6H_6$ **3** with atom labeling scheme (hydrogen atoms of ^{t}BuO groups omitted, thermal ellipsoids drawn at 30% probability).

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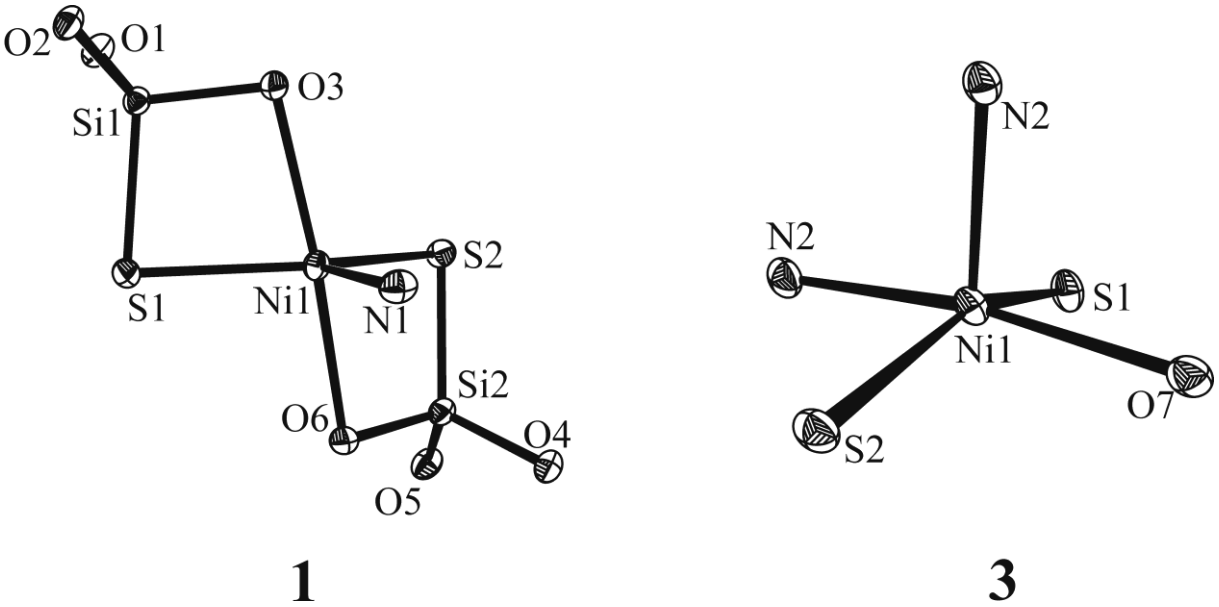

Fig 4. The comparison of geometries of **1** and **3** complexes cores (thermal ellipsoids drawn at 30% probability).

2.3 Spectral studies

The UV-Vis spectra were measured for **1** and **2** in *n*-hexane solution and Table 4 lists the electronic absorption data.

Ligands show the expected the $\pi \rightarrow \pi^*$ transitions of the aromatic rings and $n \rightarrow \pi^*$ transitions of the pyridines and silanethiolate residues in the range at about 210 - 380 nm [12, 15, 19-22, 26]. Nickel thiolates exhibit ligand-to-metal charge transfer within the range of 250 - 350 nm assigned as S → Ni LMCT [33].

The absorption spectrum of **1** and **2** in UV region exhibits intense bands at 212 nm which can be attributed to the σ(Si-S) → σ*(Si-S) transitions from tri-*tert*-butoxysilanethiolato residue [34]. Relying on our results concerning spectral analysis of cobalt(II) silanethiolates [20-22] we suppose that the band at 252 nm present in spectrum of both complexes may correspond to N-ligand → Ni CT transitions. The spectrum of **1** contains additional two less intense bands at 336 and 380 nm, which can be ascribed as S → Ni charge transfer transition of silanethiolato residue. Surprisingly, there are no such two bands present in the spectrum of **2**, which may suggests that complex **2** is not sufficiently stable in diluted solutions and undergoes dissociation. Such tendency to dissociation we observed recently for a solution of cobalt(II) complex $[Co\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ [20, 21a].

Nickel(II) complexes are numerous and many of their spectral studies have been presented in the literature. The most common are complexes with trigonal bipyramidal geometry mainly

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because of the frequent use of tripod-like ligands. The spectra of these complexes in the visible region are very characteristic, with two bands, often asymmetric with weak absorptions. Square pyramidal Ni(II) complexes are less common and their spectra in the visible region exhibit a broad band which contains at least three electronic transitions [33].

Complex **1** shows absorptions at 484 and 548 nm and a broad band at 668 nm with a shoulder at 716 nm. It may suggest that in the solution complex **1** changes its geometry from strongly distorted trigonal bipyramidal to square-pyramidal.

The neutral nickel complexes with square-planar geometry exhibit relatively weak features in the region (ca. 500-650 nm) expected for the ligand field transitions of a planar Ni(II) chromophores and are essentially transparent at lower energies. Accordingly, complex **2** shows only two absorbance bands at 508 and 576 nm.

Vibrational spectra were recorded for complexes **1** and **2** in the solid state in the range of 4000 - 700 cm^{-1}. They are similar, nevertheless some differences are visible in the region 1100 - 950 cm^{-1} (Fig. 5) with the frequencies red-shifted for complex **2**. So far, we are unable to compare currently presented spectra with other nickel(II) silanethiolates, because such spectra have not been published yet. Nevertheless, we have shown that all metal tri-*tert*-butoxysilanethiolates synthesized so far, contain superimposed bands in this range, assigned to Si–O–C bonding from silanethiolate residue. Furthermore some tri-*tert*-butoxysilanethiolate complexes of Mn(II) [18, 24], Co(II) [12, 20], Zn(II) [13, 15, 16, 22b] and Cd(II) [19, 21b, c] where oxygen atom from $-Si(O^tBu)_3$ group interacts with metal center, exhibit an additional band at about 980 cm^{-1}.

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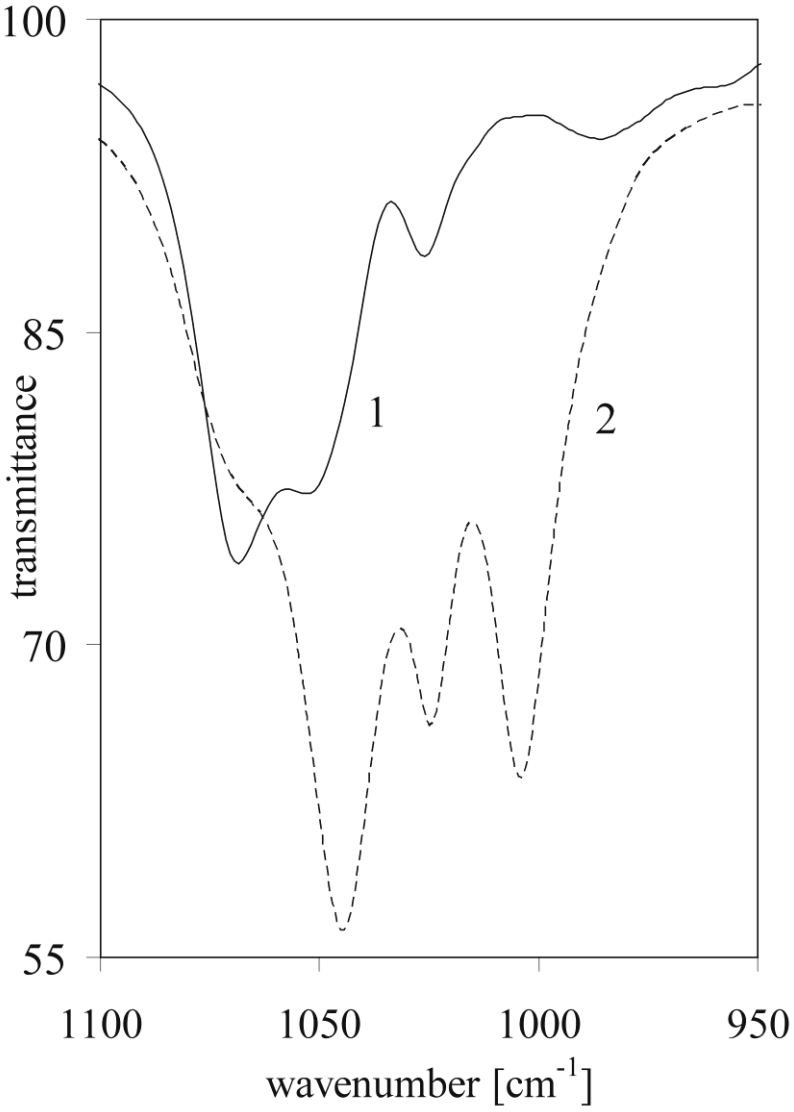

Fig 5. Solid state FT-IR spectra of complexes **1** and **2** in the range 1100 – 950 cm^{-1}.

3. Experimental

3.1 General procedures

The elemental analyses (C, H, S and N contents) were performed on an Elemental Analyser EA 1108 (Carlo Erba Instruments). Solution electronic spectra were recorded in the range 200 - 1000 nm on a Unicam SP300 spectrometer. Quartz cuvettes and *n*-hexane as solvent were used. The IR spectra were measured in the range of 4000 - 700 cm^{-1} with a Mattson Genesis II

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Gold spectrometer in KBr pellet. $(^tBuO)_3SiSH$ was prepared according to the procedure described in [25a].

3.2 Syntheses

All three complexes were obtained with the use of the same synthesis procedure. To a solution of $NiCl_2 \cdot 6H_2O$ (0.30 g, 1.25 mmol) in water (10 mL), freshly distilled base was added dropwise (5 mmol) [pyridine: 0.40 mL, **1**, 2-methylpyridine 0.49 mL, **2**, 3,5-dimethylpyridine 0.57 mL, **3**]. In each case the addition of base changed the color of the mixture from green to blue. Next the solution was stirred for 15 min and then $(^tBuO)_3SiSH$ was added (0.76 mL, 2.5 mmol). The reaction mixture was stirred for 2 hours at room temperature while green precipitate for **1** or deep-violet for **2** and **3** was formed. The product was filtered off, dissolved in 20 ml of toluene (**1** and **2**) or benzene(**3**) and dried for 2 hours with anhydrous $MgSO_4$. After filtration the solutions were concentrated to *ca*. 5 mL and left for crystallization at 4ºC.

3.2.1. $[Ni\{SSi(O^tBu)_3\}_2(C_5H_5N)]$ **1**

Violet crystals of **1** were obtained after one week. M.p. 118-120ºC; Anal. calc. for $C_{29}H_{59}NiNO_6S_2Si_2$ C, 49.94; H, 8.47; N, 2.01; S, 9.19. Found C, 50.01; H, 8.45; N, 2.00; S, 9.20%. IR (KBr) ν = 2974 (s), 2927 (s), 2900 (s, sh), 2867 (s), 1555 (w), 1540 (w), 1518 (vw), 1506 (vw), 1487 (vw), 1470 (w), 1447 (m), 1388 (m), 1364 (s), 1241 (m), 1201 (m, sh), 1184 (s), 1067 (vs), 1051 (vs, sh), 1025 (s) 984 (w, br), 816 (m), 803 (m), 791 (s, sh), 779 (m), 768 (s), 753 (s), 723 (m), 696 (m), 645 (w, sh), 635 (w), 548 (w), 530 (w), 499 (w), 470 (w, br), 420 (w).

3.2.2. $[Ni\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ **2**

Violet crystals of **2** were isolated after week. M.p. 151-152ºC; Anal. calc. for $C_{36}H_{68}NiN_2O_6S_2Si_2$ C, 53.81 H, 8.47; N, 3.48; S, 7.97. Found C, 53.71; H, 8.67; N, 3.46; S, 7.76%. IR (KBr) ν = 2972 (vs), 2928 (s), 2902 (w, sh), 2870 (w), 1610 (w), 1571 (vw), 1490 (w), 1470 (w, sh), 1461 (w), 1387 (s), 1362 (s), 1301 (vw), 1238 (s), 1206 (s), 1188 (s), 1043 (vs), 1024 (vs), 1004 (vs), 947 (vw), 909 (vw), 845 (vw), 821 (m), 800 (m), 777 (w), 762 (m),

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731 (w), 719 (w), 687 (m), 660 (w, sh), 643 (s), 580 (w), 544 (s), 511 (vw), 503 (vw), 493 (w), 477 (w), 460 (w), 451 (w), 422 (w).

3.2.3. $[Ni\{SSi(O^tBu)_3\}_2(C_7H_9N)_2(H_2O)]\cdot C_6H_6$ **3**

After one month some dark-violet crystals of **3** were obtained. M.p. 136-137ºC; Anal. calc. for $C_{44}H_{80}NiN_2O_7S_2Si_2$ C, 56.94; H, 8.69; N, 3.02; S 6.91. Found C, 53.62; H, 8.71; N, 3.29; S, 7.56%. The differences result from the evaporation of benzene and are comparable with those calculated without solvent ($C_{38}H_{74}NiN_2O_7S_2Si_2$ C, 53.77; H, 8.73; N, 3.30; S 7.55%).

3.3. X-ray

Data were collected on a KUMA KM4 diffractometer with graphite-monochromated Mo-Kα radiation using Sapphire-2 CCD detector. The apparatus was equipped with an open flow thermostat (Oxford Cryosystems) which enabled experiments at 120 K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXL program package [35]. All non-hydrogen atoms were refined anisotropically. H atoms bonded to C and O were included in calculated positions and refined as riding on their parent C atom with C–H = 0.95 Å U_{iso}(H) = 1.2 U_{eq}(C) for aromatic, C–H = 0.98 Å U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms and O–H = 0.84 and 0.85 Å U_{iso}(H) = 1.2 U_{eq}(O). Basic crystals data, descriptions of the diffraction experiment and details of the structure refinement are given in Table 1. Crystallographic data (without structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre with reference numbers CCDC 813189 - 813191 and can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Conclusion

In summary, we have prepared three novel Ni(II) tri-*tert*-butoxysilanethiolate complexes with N-heterocyclic bases as additional ligands. Complexes **1-3** were prepared with the same procedure, which provides a facile means to obtain neutral complexes with different ligand composition around metal ion and different coordination geometries: tetragonal pyramidal **1**, square-planar **2** and trigonal bipyramidal **3**. Complex **2** with NiN_2S_2 core roughly mimics nickel center in ACS/CODH active site. However its lability in solutions prompted us to put

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more efforts towards stabilization of potential biomimetic complexes. Our approach relies on synthesizing nickel silanethiolates with other type of nitrogen ligands.

Appendix A. Supplementary data

CCDC 813189 (compound 1); CCDC 813190 (compound 2); CCDC 813191 (compound 3); contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data file contains packing diagrams of compounds **1**-**3**.

References

[1] Z. Mekhalif, F. Laffineur, N. Couturier, J. Delhalle, Langmuir 19 (2003) 637-645.

[2] N. S. John, G. U. Kulkarni, A. Datta, S. K. Pati, F. Komori, G. Kavitha, C. Narayana, M. K. Sanyal, J. Phys. Chem. C 111 (2007) 1868-1870.

[3] S. A. Mirza, M. A. Pressler, M. Kumar, R. O. Day, M. J. Maroney, Inorg. Chem. 32 (1993) 977-987; V. E. Kaasjager, L. Puglisi, E. Bouwman, W. L. Driessen, J.Reedijk, Inorg. Chim. Acta 310 (2000) 183-190; V. E. Kaasjager, E. Bouwman, S. Gorter, J. Reedijk, C. A. Grapperhaus, J. H. Reibenspies, J. J. Smee, M.. Y. Darensbourg, A. Derecskei-Kovacs, L. M. Thomson, Inorg. Chem. 41 (2002) 1837-1844; B. S. Chohan, M. J. Maroney, Inorg. Chem. 45 (2006) 1906-1908; E. M. Gale, B. S. Narendrapurapu, A. C. Simmonett, H. F. Schaefer, T. C. Harrop, Inorg. Chem. 49 (2010) 7080-7096.

[4] D. Bonam, P. W. Luddent, J. Biol. Chem. 262 (1987) 2980-2987.

[5] S. E. Knowles, I. G. Jarrett, O. H. Filsell, F. J. Ballard, Biochem. J. 142 (1974) 401-411; T. I. Doukov, T. M. Iverson, J. Seravalli, S. W. Ragsdale, C. L. Drennan, Science 298 (2002) 567-572; T. C. Harrop, P. K. Mascharak, Coord. Chem. Rev. 249 (2005) 3007-3024; T. C. Harrop, M. M. Olmstead, P. K. Mascharak, Inorg. Chem. 45 (2006) 3424-3436.

[6] Y. Montet, E. Garcin, A. Volbeda, C. Hatchikians, M. Frey, J. C. Fontecilla-Camps, Pure Appl. Chem. 70 (1998) 25-31.

[7] M. J. Maroney, Curr. Opin. Chem. Biol. 3 (1999) 188-199.

[8] D. P. Barondeau, C. J. Kassmann, C. K. Bruns, J. A. Tainer, E. D. Getzoff, Biochemistry 43 (2004) 8038-8047.

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[9] P. E. Carrington, P. T. Chivers, F. Al-Mjeni, R. T. Sauer, M. J. Maroney, Nat. Struct. Biol. 10 (2003) 126-130;0 E. R. Schreiter, M. D. Sintchak, Y. Guo, P. T. Chivers, R. T. Sauer, C. L. Drennan, Nat. Struct. Biol. 10 (2003) 794-799.

[10] A. Dołęga, Coord. Chem. Rev. 254 (2010) 916-937 and references therein.

[11] I. G. Dance, Polyhedron 5 (1986) 1037-1104.

[12] B. Becker, A. Zalewska, A. Konitz, W. Wojnowski, Polyhedron 20 (2001) 2567-2576.

[13] B. Becker, A. Dołęga, A. Konitz, L. Swinder, W. Wojnowski, Z. Anorg. Allg. Chem. 627 (2001) 280-286.

[14] B. Becker, A. Pladzyk, A. Konitz, W. Wojnowski, Appl. Organometal. Chem. 16 (2002) 517-524.

[15] A. Dołęga, B. Becker, J. Chojnacki, A. Konitz, W. Wojnowski, Inorg. Chim. Acta 357 (2004) 461-467.

[16] A. Dołęga, A. Ciborska, J. Chojnacki, M. Walewski, W. Wojnowski, Thermochim. Acta 429 (2005) 103-109.

[17] A. Dołęga, A. Konitz, E. Baum, W. Wojnowski, Acta Cryst. E 61 (2005) m2582-m2584.

[18] A. Kropidłowska, J. Chojnacki, B. Becker, Polyhedron 25 (2006) 2142-2148.

[19] A. Dołęga, M. Walewski, Magn. Reson. Chem. 45 (2007) 410-415.

[20] A. Pladzyk, J. Olszewska, K. Baranowska, A. M. Dziurzyńska, Transition Met. Chem. 35 (2010) 821-827; A. Pladzyk, K. Baranowska, P. Hapter, Transition Met. Chem. 35 (2010) 373-379.

[21] a) A. Pladzyk, K. Baranowska, Acta Cryst. E 62 (2006) m2602-m2604; b) A. Dołęga, K. Baranowska, J. Gajda, S. Kaźmierski, M. Potrzebowski, Inorg. Chim. Acta 360 (2007) 2973-2982; c) A. Dołęga, K. Baranowska, Z. Jarząbek, Acta Cryst. E 64 (2008) m1515.

[22] a) A. Dołęga, A. Pladzyk, K. Baranowska, J. Jezierska, Inorg. Chim. Acta 362 (2009) 5085-5096; b) A. Dołęga, A. Pladzyk, K. Baranowska, M. Wieczerzak, Inorg. Chem. Commun. 11 (2008) 847-850.

[23] A. Dołęga, K. Baranowska, D. Gudat, A. Herman, J. Stangret, A. Konitz, M. Śmiechowski, S. Godlewska, Eur. J. Inorg. Chem. (2009) 3644-3660.

[24] a) A. Kropidłowska, J. Chojnacki, B. Becker, J. Inorg. Biochem. 101 (2007) 578-584; b) A. Kropidłowska, J. Chojnacki, B. Becker, Inorg. Chim. Acta 360 (2007) 2363-2367; c) PhD L. Aparci Plaza http://pbc.gda.pl/dlibra/docmetadata?id=2194&dirds=1&tab=1.

[25] R. Piękoś, W. Wojnowski, Z. Anorg. Allg. Chem. 318 (1962) 212-216; A. Herman, B. Becker, W. Wojnowski, Z. Anorg. Allg. Chem. 450 (1979) 178-182.

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[26] A. Pladzyk, K. Baranowska, D. Gudat, S. Godlewska, M. Wieczerzak, J. Chojnacki, M. Bulman, K. Januszewicz, A. Dołęga, Polyhedron 30 (2011) 1191-1200.

[27] M. L. Golden, M. V. Rampersad, J. H. Reibenspies, M. Y. Darensbourg, Chem. Commun. (2003) 1824-1825; Ş. Güveli, T. Bal-Demirci, N. Özdemir, B. Ülküseven, Transiton Met. Chem. 34 (2009) 383-388; R. M. Jenkins, M. L. Singleton, E. Almaraz, J. H. Reibenspies, M. Y. Darensourg, Inorg. Chem. 48 (2009) 7280-7293; A. Esparza-Ruiz, G. González-Gómez, E. Mijangos, A. Peña-Hueso, H. López-Sandoval, A. Flores-Parra, R. Contreras, N. Barba-Behrens, Dalton Trans. 39 (2010) 6302-6309.

[28] L. M. Amzel, S. Baggio, L. N. Becka, J. Chem. Soc. A (1969) 266-272; I. Solacolu, D. Sandulescu, C. Dragulescu, Rev. Roum. Chim. 19 (1974) 415; M. H. Moore, L. R. Nassimbeni, M. L. Niven, Inorg. Chim. Acta 132 (1987) 61-66; A. L. Spek, J. Kolnaar, J. Reedijk, Priv. Commun. (2004); T. L. Tao, C. G. Riodan, G. P. A. Yap, Priv. Commun. (2007).

[29] P. S. Shetty, Q. Fernando, J. Am. Chem. Soc. 92 (1970) 3964-3969; C. P. Bhasin, R. Bohra, G. Srivastava, R. C. Mehrotra, P. B. Hitchcock, Inorg. Chim. Acta 164 (1989) 11-16; N. Baidya, M. M. Olmstead, P. K. Mascharak, J. Am. Chem. Soc. 114 (1992) 9666-9668; N. Baidya, M. M. Olmstead, J. P. Whitehead, C. Bagyinka, M. J. Maroney, P. K. Mascharak, Inorg. Chem. 31 (1992) 3612-3619; M. L. Golden, S. P. Jeffery, M. L. Miller, J. H. Reibenspies, M. Y. Darensbourg, Eur. J. Inorg. Chem. (2004) 231-236; T. Fritz, G. Steinfeld, S. Kass, B. Kersting, Dalton Trans. (2006) 3812-3821; A. L. Bingham, J. E. Drake, M. B. Hursthouse, M. E. Light, M. Nirwan, R. Ratnani, Polyhedron 26 (2007) 2672-2678; S. Pfirrmann, C. Limberg, E. Hoppe, Z. Anorg. Allg. Chem. 635 (2009) 312-316.

[30] A. W. Addison, T. N Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349-1356.

[31] L. Yang, D. R. Powell, R. P. Houser, Dalton Trans. (2007) 955-964.

[32] V. Mathrubootham, J. Thomas, R. Staples, J. McCraken, J. Shearer, E. L. Hegg, Inorg. Chem. 49 (2010) 5393-5406.

[33] A. B. P. Lever, Inorganic Electronic Spectroscopy, second ed., Elsevier Science Publishing Co., Inc., New York, 1984.

[34] A. Herman, B. Dręczewski, W. Wojnowski, J. Organomet. Chem. 339 (1988) 41-49.

[35] G. M. Sheldrick, Acta Crystallogr Sect A Found Crystallogr. 64 (2008) 112-122.

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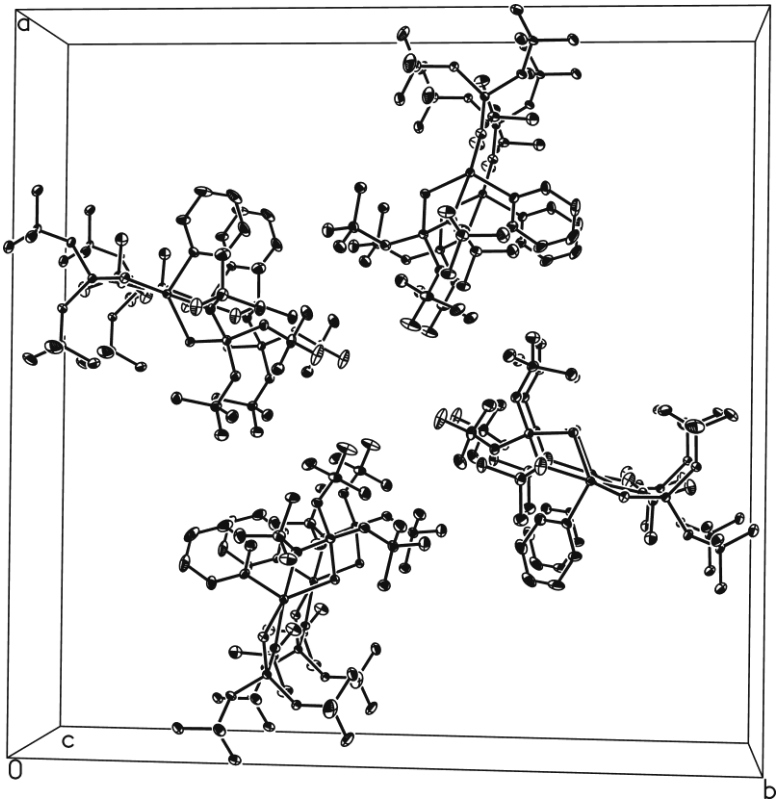

Fig 1S. View through the c axis in the cell of **1**. Thermal ellipsoids drawn at 30% probability.

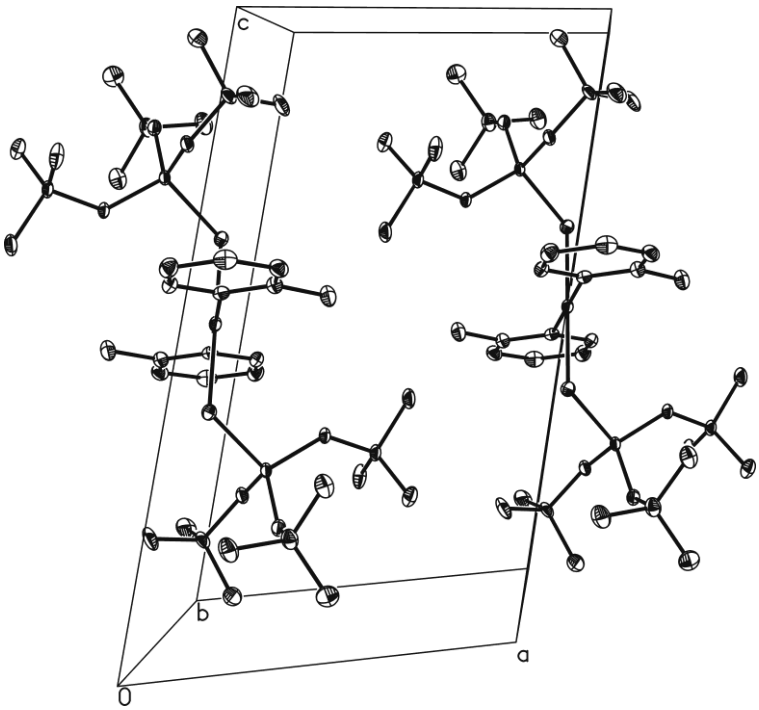

Fig 2S. View through the b axis in the cell of **2**. Thermal ellipsoids drawn at 30% probability.

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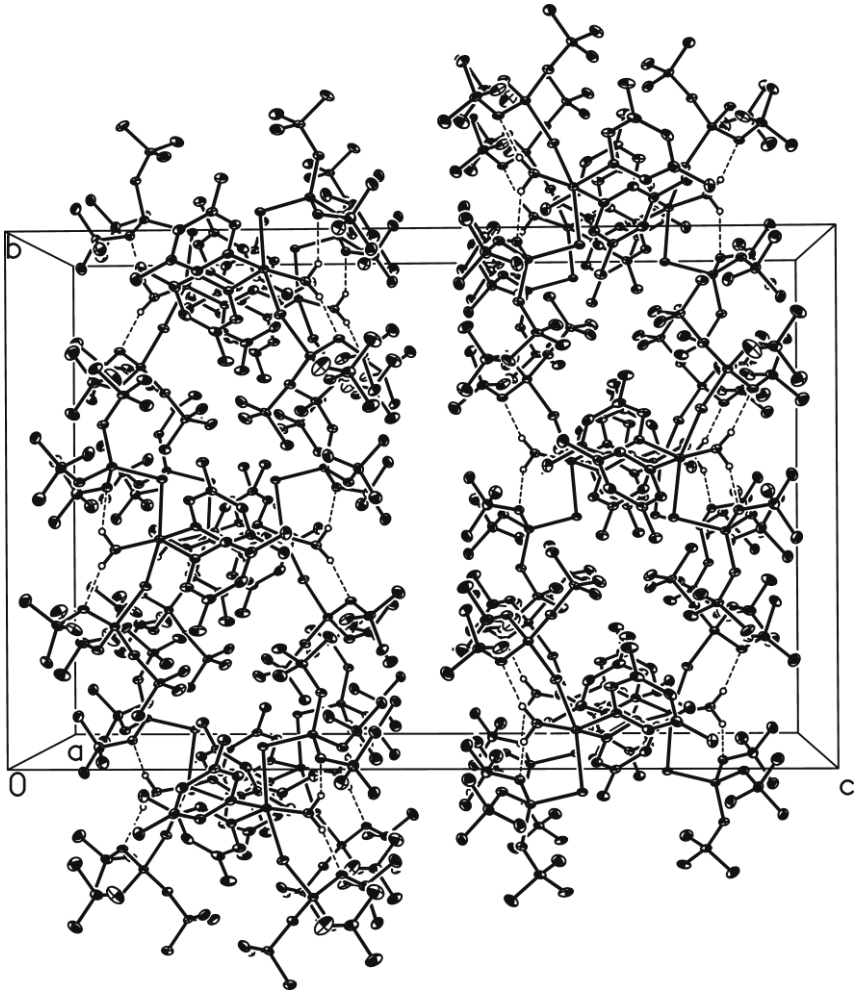

Fig 3S. View through the a axis in the cell of **3**. Thermal ellipsoids drawn at 30% probability.

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Table 1. Crystal data and structure refinement for **1-3** complexes.

	1	**2**	**3**
Empirical formula	$C_{29}H_{59}NiNO_6S_2Si_2$	$C_{36}H_{68}NiN_2O_6S_2Si_2$	$C_{44}H_{80}NiN_2O_7S_2Si_2$
Formula weight	696.78	803.93	928.11
T (K)	120(2)	120(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	tetragonal	triclinic	orthorhombic
Space group	*I4*	*P*-1	*Pbca*
Unit cell dimensions			
a (Å)	29.900(4)	9.1388(6)	16.1204(4)
b (Å)	29.900(4)	9.4625(6)	20.5424(4)
c (Å)	8.8450(18)	14.6865(11)	31.5906(11)
α (º)	90	77.324(6)	90
β (º)	90	75.767(6)	90
γ (º)	90	62.410(7)	90
V (Å^3)	7908(2)	1082.78(13)	10461.3(5)
Z	8	1	8
$\boldsymbol{\rho}_{calc}$ (g/cm^3)	1.171	1.233	1.179
μ (mm^{-1})	0.692	0.641	0.541
F(0 0 0)	3008	434	4016
Crystal size (mm)	0.21 x 0.18 x 0.14	0.45 x 0.07 x 0.04	0.20 x 0.15 x 0.09
θ Range (º)	2.0395-32.4692	2.4400-32.3144	2.0550-32.5425
Index ranges	$-30 \le h \le 38$ $-38 \le k \le 37$ $-11 \le h \le 11$	$-7 \le h \le 10$ $-10 \le k \le 11$ $-17 \le h \le 17$	$-12 \le h \le 21$ $-27 \le k \le 27$ $-41 \le h \le 41$
Reflections collected	31523	6368	79318
Independent reflections	8572	3670	12617
R_{int}	0.0350	0.0460	0.1385
Completeness to theta	26.99° (99.8%)	25.00° (96.4%)	28.00° (99.9%)
Refinement method		Full-matrix least-squares on F^2	
Parameters	388	233	529
S (Goodness-of-fit)	1.16	1.119	1.101
R_1 [I > 2σ(I)]	R_1 = 0.0389 wR_2 = 0.0946	R_1 = 0.0542 wR_2 = 0.1377	R_1 = 0.0864 wR_2 = 0.2100
R indices (all data)	R_1 = 0.0482 wR_2 = 0.0979	R_1 = 0.0812 wR_2 = 0.1662	R_1 = 0.1678 wR_2 = 0.2533
Largest differences peak and hole (e Å^{-3})	0.694 and -0.944	0.625 and -0.898	1.430 and -0.970

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Table 2. Selected bond lengths (Å) and angles (°) for complexes **1**-**3**.

	1	**2**	**3**
Bond lengths			
Ni1–N1	2.025(2)	1.907(3)	2.048(5)
Ni1–N2	-	-	2.069(5)
Ni1–S1	2.302(8)	2.253(2)	2.385(4)
Ni1–S2	2.311(8)	-	2.420(4)
Ni1–O3	2.239(9)	-	-
Ni1–O6	2.269(9)	-	-
Ni1–O7	-	-	2.095(4)
S1–Si1	2.075(2)	2.097(5)	2.068(2)
S2–Si2	2.071(2)		2.050(2)
Si1–O1	1.622(2)	1.630(3)	1.659(4)
Si1–O2	1.633(2)	1.627(3)	1.631(4)
Si1–O3	1.665(2)	1.638(3)	1.632(4)
Si2–O4	1.635(2)	-	1.647(4)
Si2–O5	1.623(2)	-	1.657(4)
Si2–O6	1.662(2)	-	1.629(4)
Bond angles			
N(1)– Ni(1)–N(2)	-	180.00(10)[i]	96.78(19)
N(1)–Ni(1)–S(1)	110.61(8)	85.45(10)	106.83(13)
N(1)–Ni(1)–S(2)	108.53(8)	94.55(10)[i]	93.91(13)
N(2)–Ni(1)–S(1)	-	94.55(10)[i]	84.28(13)
N(2)–Ni(1)–S(2)	-	85.45(10)[i]	90.58(13)
S(1)–Ni(1)–S(2)	140.74(3)	180.00(18)[i]	159.07(6)
Si(1)–S(1)–Ni(1)	84.25(4)	111.71(5)	117.74(8)
Si(2)–S(2)–Ni(1)	84.21(3)	-	04.83(7)
S(1)–Ni(1)–O(3)	78.30(5)	-	-
S(1)–Ni(1)–O(6)	97.69(5)	-	-
N(1)–Ni(1)–O(3)	94.41(8)	-	-
N(2)–Ni(1)–O(6)	91.54(8)	-	-
O(3)–Ni(1)–O(6)	173.71(7)	-	-
O(7)–Ni(1)–N(1)	-	-	92.83(17)
O(7)–Ni(1)–N(2)	-	-	170.37(18)
O(7)–Ni(1)–S(1)	-	-	92.19(12)
O(7)–Ni(1)–S(2)	-	-	89.55(12)

[i] - symmetry codes: 2 – x, 1 – y, 1 – z

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Table 3. Hydrogen bond lengths (Å) and angles (°) for **3**.

D-H···A	D–H	H···A	D···A	∠ D–H···A
O7–H 7D···O5	0.84(2)	2.03(2)	2.859(5)	168(6)
O7–H 7F···O1	0.85(2)	1.91(3)	2.743(6)	164(7)

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Table 4. Summary of electronic spectra of complexes **1** and **2**.

	UV-vis: λ_{max} (nm) (ε, $M^{-1}cm^{-1}$)	
	1	**2**
CT transitions	212 (7126) 252 (5870) 336 (1272) 380 (1768)	212 (7126) 252 (5870)
d $\rightarrow$ d transitions	484 (154) 548 (140) 668 (89) 716sh (75)	504 (52) 576 (55)

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