Polyhedron 30 (2011) 2400–2405

Contents lists available at ScienceDirect

Polyhedron

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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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ARTICLE INFO

*Article history:*
Received 19 May 2011
Accepted 15 June 2011
Available online 7 July 2011

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

## ABSTRACT

Three heteroleptic, neutral nickel(II) tri-*tert*-butoxysilanethiolates with monodentate heterocyclic bases (pyridine, 2-methylpyridine and 3,5-dimethylpyridine) serving as additional ligands have been prepared following the same synthetic procedure. The 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 recorded.

Three different coordination motifs have been observed in these complexes. 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. The 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 $NiN_2OS_2$ environment. Complex **2** roughly mimics one of the two metal centers in the active site of the ACS/CODH enzyme.

## 1. Introduction

Nickel complexes with a 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 conversion to S-bonded sulfinato complexes by the incorporation of dioxygen [3–7].

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) [8], which interconverts CO and $CO_2$, and acetyl-coenzyme A synthase/carbon monoxide dehydrogenase (ACS/CODH) [9–12], which converts CO gas into a carbon source. NiFe hydrogenase catalyzes the reversible oxidation of hydrogen gas [13].

Nickel proteins present diverse types of coordination modes on the metal ion, however general insight into four nickel-binding sites that have been so far identified in enzymatic structures shows the tendency to adopt a square-planar geometry on the metal ion [14]. For instance, nickel superoxide dismutase (NiSOD) in the fully reduced form contains Ni(II) with a square planar geometry. The oxidation state changes to Ni(III) and the spatial arrangement around the metal ion to square pyramidal when the enzyme is in a resting state [15]. The transcription factor NikR, which plays a role of a cytoplasmic nickel sensor in *Escherichia coli* and *Helicobacter pylori*, is built up 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 the *apo* form suggests that the role of nickel is crucial for the proper conformation and activity of the protein [16,17].

A large number of studies devoted to nickel proteins are dedicated to the analysis of the structure of the A-cluster active site of ACS/CODH enzyme. This particular protein attracts attention because of its significant role in the global carbon cycle. The active site of the A-cluster of ACS/CODH consists of a $Fe_4S_4$ cubane bridged by a cysteine thiolate to a dinuclear $M(\mu\text{-}S)M'$ cluster where M is nickel and M′ may be Ni(II), Zn(II) or Cu(I). The coordination of the nickel center is completed by two backbone carboxamido nitrogen atoms, resulting in a $NiN_2S_2$ square-planar arrangement [9–12].

In recent years, our work has been targeted towards biomimetic studies and the prevalent part of these was devoted to zinc thiolates [18]. Now we have turned our attention to nickel complexes with S-thiolate and N-donor ligands that may serve as biomimetic models for the active sites of nickel-containing proteins.

The synthesis of transition metal complexes with thiolate ligands presents some difficulties because of the strong bridging tendency of thiolate sulfur, leading to the formation of oligo- and polymeric species [19]. One of the strategies which help to avoid

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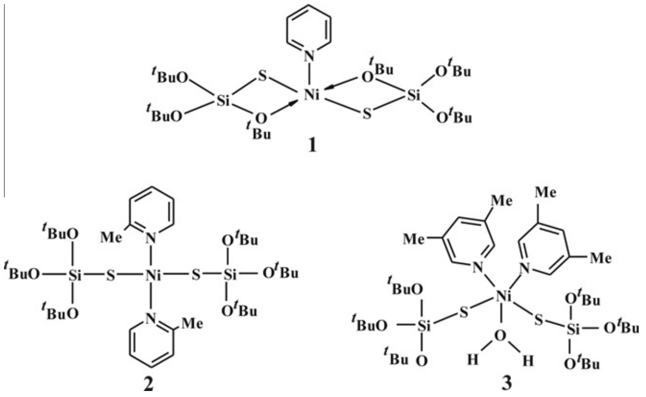
doi:10.1016/j.poly.2011.06.028



**Scheme 1.** Obtained complexes **1**–**3**.

such undesirable side processes 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, when used as a source of a very bulky thiolate ligand, clearly reduces the tendency of sulfur promoted polymerization and allowed us to obtain numerous mono- and binuclear heteroleptic silanethiolate complexes [20–33]. Moreover, unlike many others, this particular silanethiol is resistant towards hydrolysis, and so the syntheses may be carried out under atmospheric conditions [34,35]. 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) [26,33]. In some complexes, the immediate environment on the metal center follows that found in the active site of alcohol dehydrogenase (ADH) [32,33a], and one complex, $[Zn\{SSi(O^tBu)_3\}_2(C_7H_9NO)]$, was tested for its catalytic properties [36]. We have also affirmed that some heteroleptic cobalt(II) tri-*tert*-butoxysilanethiolates are isomorphous to the related zinc(II) complexes and can be considered as spectral models of ADH protein in solution [31].

So far the majority of nickel(II) thiolates serving as structural mimics of the active sites of NiSOD, NikR and ACS/CODH enzymes employ N, S ligands of the chelating type [37–40]. Only a few examples of Ni(II) complexes with monodentate N- and S-ligands are known [41–45]. For these 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 a $NiN_2S_2$ core, related to the coordination mode present in ACS/CODH protein. In this paper we report the 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).

## 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, the 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 a ligand and HCl acceptor. Water insoluble products were collected and recrystallized from organic solvents. Complexes **1** and **2** are stable and can be stored under atmospheric conditions for months, in contrast to the unstable complex **3**. The bases used for the syntheses were chosen because of their different basicities (p$K_a$: 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 a 1:2 molar ratio of nitrogen and sulfur, and thus two silanethiolate residues and one pyridine molecule coordinated to the metal ion. Also the FT-IR solid state spectrum of **1** showed the presence of frequencies typical for a heterocyclic base and Si–O–C bonding from the silanethiolate residue. The composition and structure of the complex was finally established with the use of X-ray analysis, showing the metal ion was coordinated by one molecule of pyridine and two O, S-chelating silanethiolato residues in a $NiNO_2S_2$ type of arrangement. Such a type of complex was synthesized previously for Co(II) and Zn(II) [20,21,23,24].

The exchange of pyridine for more basic and more sterically hindered 2-methylpyridine gave another product with the 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 single crystal X-ray crystallography. Surprisingly, unlike **1**, we found in **2** two N-donor ligands within the Ni(II) coordination sphere. This was accompanied by a change of bonding mode of both tri-*tert*-butoxysilanethiolato ligands from chelating in **1** to strictly monodentate in **2**, and thus the formation of a $NiN_2S_2$ central core. Syntheses performed previously for Co(II) and Zn(II) tri-*tert*-butoxysilanethiolates with the same pyridine derivative resulted, amongst others, in the penta-coordinated $[M\{SSi(O^tBu)_3\}_2(C_6H_7N)]$ [20,32].

Finally, we used 3,5-dimethylpyridine and following the same synthetic procedure once more obtained another type of product – deep violet crystals of the complex $[Ni\{SSi(O^tBu)_3\}_2(C_7H_9N)_2(H_2O)(C_6H_6)]$ (**3**). Its structure was solved by X-ray crystallography, revealing Ni(II) coordinated by two monodentate silanethiolato residues, two N-donor bases and one water molecule, with the central core adopting a $NiN_2OS_2$ form. We have noticed that at room temperature after a short period of time the crystals become opaque, which may be caused by evaporation of the solvent from this sample or it may suggest degradation of the complex. Heteroleptic tri-*tert*-butoxysilanethiolates of Co(II) and Zn(II) with 3,5-dimethylpyridine as an additional ligand have been prepared by us previously [20,27–29], but in both cases they had the formula $[M\{SSi(O^tBu)_3\}_2(C_7H_9N)]$ 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 the atom labeling schemes and their crystal packing are illustrated in Figs. 1–4 and 1S–3S (Supplementary data). Selected bond lengths and angles are listed in Table 2. In order to estimate the geometric shape of the obtained complexes, the Addison angular structural parameter ($\tau$) has been calculated [54,55]. For four and five-coordinate complexes the parameters $\tau_4$ and $\tau_5$, respectively are defined as $\tau_4 = [360° - (\alpha - \beta)]/141°$ and $\tau_5 = (\alpha - \beta)/60°$, where $\alpha$ and $\beta$ are the largest bond angles in the complex. For complexes with coordination number CN = 5, $\tau_5$ becomes unity for a perfect trigonal bipyramidal geometry and $\tau_5 = 0$ for a tetragonal pyramid [54]. For four coordinated complexes a perfect square planar geometry leads to $\tau_4 = 0$ and a tetrahedral geometry to $\tau_4 = 1$ [55].

Crystals of complex **1** consist of eight molecules in the 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

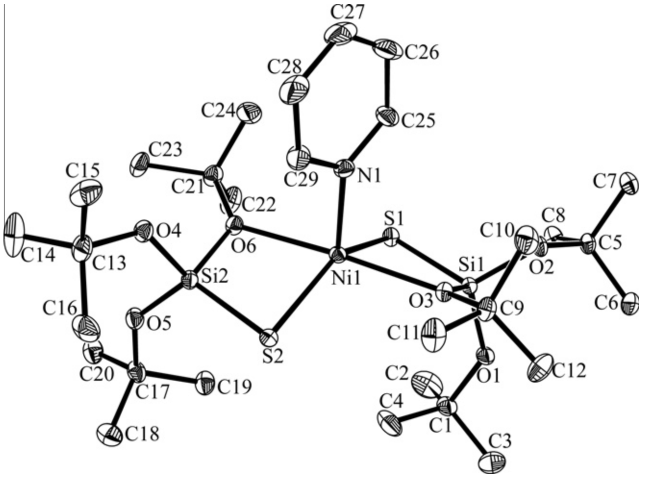


**Fig. 1.** Molecular structure of [Ni{SSi(O$^t$Bu)$_3$}$_2$(C$_5$H$_5$N)] **1** with the atom labeling scheme (hydrogen atoms of $^t$BuO groups are omitted, thermal ellipsoids are drawn at 30% probability).

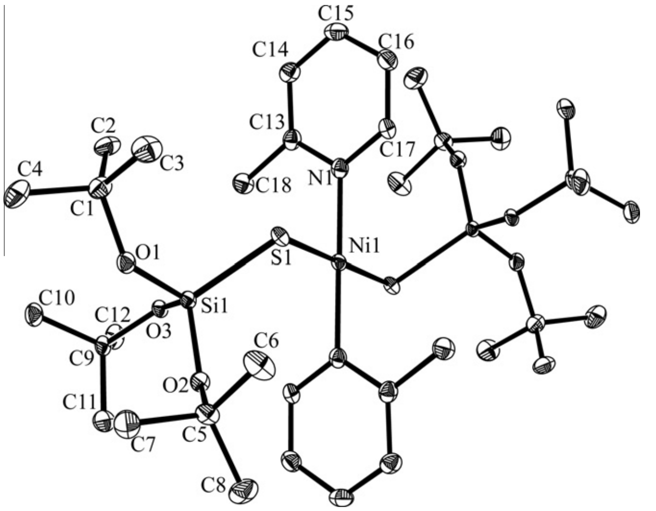


**Fig. 2.** Molecular structure of [Ni{SSi(O$^t$Bu)$_3$}$_2$(C$_6$H$_7$N)$_2$] **2** with the atom labeling scheme ($^t$Bu groups and hydrogen atoms of the aromatic ring are omitted for clarity, thermal ellipsoids are drawn at 30% probability).

silanethiolate residues, and one N atom of pyridine. The parameter $\tau_5$ calculated for complex **1** has a value of 0.55 and thus its geometry is unequivocal, being about halfway between a square pyramid and a trigonal bipyramid, albeit slightly closer to the latter, with the 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 the ($^t$BuO)$_3$SiS residue behaves as a bidentate ligand [20,24,27–30].

Complex **2** crystallizes with one molecule in the unit cell (Figs. 2 and 2S). Although the geometry of its NiN$_2$S$_2$ core may be approximated as square-planar ($\tau_4 = 0$) with the S1–Ni1–S2 and N1–Ni1–N2 angles being the ideal value of 180°, the two N–Ni–S angles differ by ca. 10°. The Ni–S bond distance of 2.253(2) Å in **2** is slightly longer than those found in square-planar NiN$_2$S$_2$ complexes with scorpionate-type N$_2$S$_2$ ligands [9–12].

Complex **3** crystallizes with eight molecules in the unit cell (Figs. 3 and 3S). The nickel coordination sphere contains five independent ligands – two silanethiolate residues, two molecules of 3,5-dimethylpyridine and one molecule of water, which form a

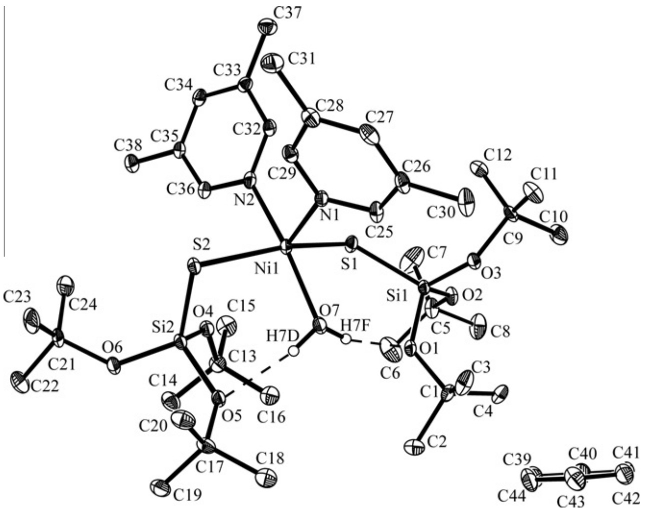


**Fig. 3.** Molecular structure of [Ni{SSi(O$^t$Bu)$_3$}$_2$(C$_7$H$_9$N)$_2$(H$_2$O)]·C$_6$H$_6$ **3** with the atom labeling scheme (hydrogen atoms of $^t$BuO groups are omitted, thermal ellipsoids are drawn at 30% probability).

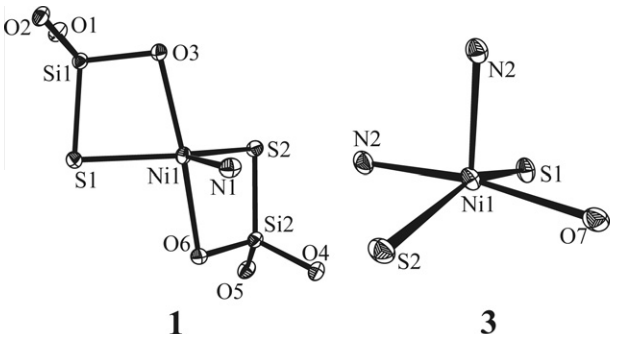


**Fig. 4.** A comparison of the geometries of the cores of complexes **1** and **3** (thermal ellipsoids are drawn at 30% probability).

NiN$_2$OS$_2$ kernel. The Addison parameter $\tau_5$ presents a value of 0.18. Hence, the geometry is a definitely closer to a square pyramid than to a trigonal bipyramid, but it is far from a perfect one. The base of the pyramid is formed by two S atoms, an O atom from water and a N atom from one of the 3,5-dimethylpyridines, while the second N-base molecule forms the peak of the pyramid (Fig. 4). The nickel atom deviates by 0.301 Å from the basal plane. The bond lengths found in complex **3** are similar to those found in complex **1** and other penta-coordinated nickel thiolate complexes [46–53]. The 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 the 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.

### 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. The ligands show the expected the $\pi \rightarrow \pi^*$ transitions of aromatic rings and $n \rightarrow \pi^*$ transitions of the pyridines and silanethiolate residues in the range 210–380 nm [20,23,27–31,36]. Nickel thiolates exhibit ligand-to-metal charge transfer within the range 250–350 nm, assigned as S → Ni LMCT [56,57].

The absorption spectra of **1** and **2** in the UV region exhibit intense bands at 212 nm which can be attributed to the $\sigma$(Si–S) → $\sigma^*$(Si–S)

**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) |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | tetragonal | triclinic | orthorhombic |
| Space group | $I4$ | $P\bar{1}$ | $Pbca$ |
| *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) |
| $\alpha$ (°) | 90 | 77.324(6) | 90 |
| $\beta$ (°) | 90 | 75.767(6) | 90 |
| $\gamma$ (°) | 90 | 62.410(7) | 90 |
| $V$ (Å$^3$) | 7908(2) | 1082.78(13) | 10461.3(5) |
| $Z$ | 8 | 1 | 8 |
| $\rho_{calc}$ (g/cm$^3$) | 1.171 | 1.233 | 1.179 |
| $\mu$ (mm$^{-1}$) | 0.692 | 0.641 | 0.541 |
| $F$(0 0 0) | 3008 | 434 | 4016 |
| Crystal size (mm) | 0.21 × 0.18 × 0.14 | 0.45 × 0.07 × 0.04 | 0.20 × 0.15 × 0.09 |
| $\theta$ Range (°) | 2.0395–32.4692 | 2.4400–32.3144 | 2.0550–32.5425 |
| Index ranges | $-30 \leqslant h \leqslant 38$<br>$-38 \leqslant k \leqslant 37$<br>$-11 \leqslant h \leqslant 11$ | $-7 \leqslant h \leqslant 10$<br>$-10 \leqslant k \leqslant 11$<br>$-17 \leqslant h \leqslant 17$ | $-12 \leqslant h \leqslant 21$<br>$-27 \leqslant k \leqslant 27$<br>$-41 \leqslant h \leqslant 41$ |
| Reflections collected | 31 523 | 6368 | 79 318 |
| Independent reflections | 8572 | 3670 | 12 617 |
| $R_{int}$ | 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 |
| $R_1$ [$I > 2\sigma(I)$] | $R_1 = 0.0389$<br>$wR_2 = 0.0946$ | $R_1 = 0.0542$<br>$wR_2 = 0.1377$ | $R_1 = 0.0864$<br>$wR_2 = 0.2100$ |
| $R$ indices (all data) | $R_1 = 0.0482$<br>$wR_2 = 0.0979$ | $R_1 = 0.0812$<br>$wR_2 = 0.1662$ | $R_1 = 0.1678$<br>$wR_2 = 0.2533$ |
| Largest differences in peak and hole (e Å$^{-3}$) | 1.430 and −0.970 | 0.694 and −0.944 | 0.625 and −0.898 |

transitions from the tri-*tert*-butoxysilanethiolato residue [58]. Relying on our results concerning the spectral analysis of cobalt(II) silanethiolates [28–31], we suppose that the band at 252 nm present in the spectra of both complexes may correspond to N-ligand → Ni CT transitions. The spectrum of **1** contains additionally two less intense bands at 336 and 380 nm, which can be ascribed as S → Ni charge transfer transitions of the 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. We recently observed such a tendency to dissociate for a solution of the cobalt(II) complex $[Co\{SSi(O^tBu)_3\}_2(C_6H_7N)_2]$ [28–30a].

Nickel(II) complexes are numerous and many of their spectral studies have been presented in the literature. The most common are complexes with a trigonal bipyramidal geometry, mainly 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 [57].

**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: $2 - x, 1 - y, 1 - z$.

**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) |

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

| UV–Vis: $\lambda_{max}$ (nm) ($\varepsilon$, M$^{-1}$ cm$^{-1}$) | **1** | **2** |
|---|---|---|
| CT transitions | 212 (7126)<br>252 (5870)<br>336 (1272)<br>380 (1768) | 212 (7126)<br>252 (5870) |
| d → d transitions | 484 (154)<br>548 (140)<br>668 (89)<br>716sh (75) | 504 (52)<br>576 (55) |

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

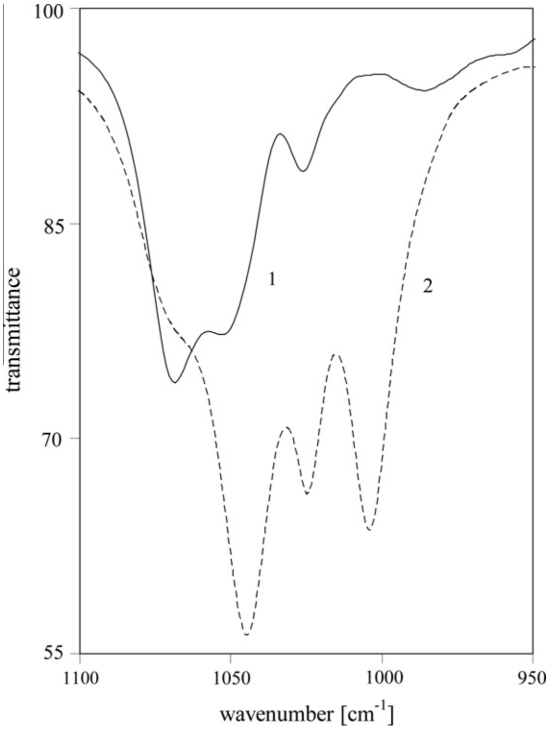


**Fig. 5.** Solid state FT-IR spectra of complexes **1** and **2** in the range 1100–950 cm$^{-1}$.

Vibrational spectra were recorded for complexes **1** and **2** in the solid state in the range 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 have been unable to compare the currently presented spectra with other nickel(II) silanethiolates, because such spectra have not been published yet. Nevertheless, we have shown that all the metal tri-*tert*-butoxysilanethiolates synthesized so far contain superimposed bands in this range, assigned to Si–O–C bonding from the silanethiolate residue. Furthermore some tri-*tert*-butoxysilanethiolate complexes of Mn(II) [26,33], Co(II) [20,28,29], Zn(II) [21,23,24,31b] and Cd(II) [27,30b,c], where the oxygen atom from the –Si(O$^t$Bu)$_3$ group interacts with the metal center, exhibit an additional band at about 980 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 4000–700 cm$^{-1}$ with a Mattson Genesis II Gold spectrometer in KBr pellets. ($^t$BuO)$_3$SiSH was prepared according to the procedure described in [34].

### 3.2. Syntheses

All three complexes were obtained using 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 ($^t$BuO)$_3$SiSH was added (0.76 mL, 2.5 mmol). The reaction mixture was stirred for 2 h at room temperature, during which time a 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 h with anhydrous $MgSO_4$. After filtration the solutions were concentrated to ca. 5 mL and left for crystallization at 4 °C.

#### 3.2.1. [Ni{SSi(O$^t$Bu)$_3$}$_2$(C$_5$H$_5$N)] *1*

Violet crystals of **1** were obtained after 1 week. M.p. 118–120 °C; *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) $\nu$: 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$^t$Bu)$_3$}$_2$(C$_6$H$_7$N)$_2$] *2*

Violet crystals of **2** were isolated after a week. M.p. 151–152 °C; *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) $\nu$: 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), 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$^t$Bu)$_3$}$_2$(C$_7$H$_9$N)$_2$(H$_2$O)]·C$_6$H$_6$ *3*

After 1 month some dark-violet crystals of **3** were obtained. M.p. 136–137 °C; *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 K$\alpha$ radiation using a Sapphire-2 CCD detector. The apparatus was equipped with an open flow thermostat (Oxford Cryosystems) which enabled experiments to be carried out 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 [59]. 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 crystal data, descriptions of the diffraction experiment and details of the structure refinement are given in Table 1.

## 4. 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 using the same procedure, which provides a facile means to obtain neutral complexes with a different ligand composition around the metal ion and different coordination geometries: tetragonal pyramidal **1**, square-planar **2** and trigonal bipyramidal **3**. Complex **2**, with a $NiN_2S_2$ core, roughly mimics the nickel center in the ACS/CODH active site. However its lability in solutions prompted us to put more effort towards the stabilization of potential biomimetic complexes. Our approach relies on synthesizing nickel silanethiolates with other types of nitrogen ligands.

## Appendix A. Supplementary data

CCDC 813189, 813190 and 813191 contains the supplementary crystallographic data for (**1**), (**2**) and (**3**). 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 associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.06.028.

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