

Cobalt(II) silanethiolato complexes with dimethylpyridines: crystal structures and spectroscopic studies

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Abstract Cobalt(II) tri-*tert*-butoxysilanethiolates with 2,5-dimethylpyridine, 3,4-dimethylpyridine and 3,5-dimethylpyridine co-ligands have been synthesized by reaction of bimetallic $[\text{Co}\{\mu\text{-SSi}(\text{O}^t\text{Bu})_3\}\{\text{SSi}(\text{O}^t\text{Bu})_3\}(\text{NH}_3)_2]$ with the appropriate pyridines. The complexes were characterized by elemental analysis, single-crystal X-ray structure determination, IR and UV–Vis spectroscopy. These complexes are tetra- or penta-coordinated with CoN_2S_2 and CoNO_2S_2 cores, respectively.

Introduction

Transition metal silanethiolates (MSSiR_3) have recently attracted much attention owing to their potential applications as precursors in sulfido cluster-forming reactions, thin layer fabrication and catalysis [1–5]. Generally, silanethiols are sensitive to atmospheric conditions and hydrolyze easily with the evolution of H_2S . In our syntheses, we use tri-*tert*-butoxysilanethiol as a source of *S*-ligand. This sterically hindered compound is resistant to hydrolysis and enables the preparation of monomeric and relatively stable complexes for synthesis conducted under normal atmospheric conditions [6–10].

Our goal is to design complexes that can act as molecular models for biological systems, both in the solid state and in the solution. Previous results indicate that Co(II) and Zn(II) tri-*tert*-butoxysilanethiolates show strong correlations with biological systems and imitate the coordination

environment of metal-containing proteins like alcohol dehydrogenase ADH, transcription factor TFIIIA or farnesyltransferase FTase, where the metal atom is coordinated by histidines and cysteines [6–14].

Owing to the structural and chemical similarity of Co(II) and Zn(II) silanethiolates, we plan to synthesize a series of cobalt(II) tri-*tert*-butoxysilanethiolates, with additional N donor ligands, in order to elaborate their spectroscopic and structural properties. Relying on our earlier UV–Vis analysis of cobalt(II) silanethiolates with imidazoles as a co-ligand [10], we suppose that such models will be useful for the spectral studies of the active centers of other metalloproteins [10, 15–18], and this paper is the continuation of our research. Here, we describe the syntheses, structures and spectral analysis of three monomeric new cobalt(II) tri-*tert*-butoxysilanethiolates with dimethylpyridine co-ligands.

Experimental

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 on a Unicam SP300 spectrometer in *n*-hexane in the range 200–800 nm. Quartz cuvettes and *n*-hexane as solvent were used. The IR spectra were measured for crystalline compounds in the range of $4,000\text{--}700\text{ cm}^{-1}$ with a Momentum microscope (IR detector) attached to a Mattson Genesis II Gold spectrometer (IR source).

Syntheses

Tri-*tert*-butoxysilanethiol and $[\text{Co}\{\mu\text{-SSi}(\text{O}^t\text{Bu})_3\}\{\text{SSi}(\text{O}^t\text{Bu})_3\}(\text{NH}_3)_2]$ were obtained according to procedures

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described previously [13, 19]. All other reagents were obtained commercially. Amines were dried by standard methods and distilled prior to use.

All three complexes were obtained using the same synthesis procedure. To a solution of $[\text{Co}\{\mu\text{-SSi}(\text{tBuO})_3\}\{\text{SSi}(\text{tBuO})_3\}(\text{NH}_3)_2]$ (0.25 g, 0.2 mmol) in *n*-hexane (10 mL), freshly prepared base was added dropwise (2,5-dimethylpyridine: 46.3 μL , 0.4 mmol **1**, 3,5-dimethylpyridine: 116 μL , 1 mmol **2**, 3,4-dimethylpyridine: 116 μL , 1 mmol **3**). After gentle stirring for a few minutes, the mixtures were allowed to stand at 4 °C to yield crystals of the complexes.

$[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(2,5\text{-dimethylpyridine})]$ **1** Crystals are very stable in atmospheric conditions. *Anal.* Found for $\text{C}_{31}\text{H}_{63}\text{NO}_6\text{S}_2\text{Si}_2\text{Co}$: C 51.4, H 8.8, N 2.1, S 9.0%. Calc. C 51.3, H 8.8, N 2.0, S 8.8%. M. p. at 172–173 °C.

$[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(3,5\text{-dimethylpyridine})(\text{NH}_3)]$ **2** is unstable at room temperature and after some hours changes color from blue to pink-violet. *Anal.* Found for $\text{C}_{31}\text{H}_{66}\text{N}_2\text{O}_6\text{S}_2\text{Si}_2\text{Co}$: C 50.8, H 8.6, N 3.7, S 8.8%. Calc. C 50.2, H 8.9, N 3.8, S 8.6%. M. p. at 132–134 °C.

$[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(3,4\text{-dimethylpyridine})_2]$ **3** is also unstable just as complex **2**. *Anal.* Found for $\text{C}_{38}\text{H}_{72}\text{N}_2\text{O}_6\text{S}_2\text{Si}_2\text{Co}$: C 54.1, H 8.8, N 2.9, S 8.0%. Calc. C 54.8, H 8.7, N 3.4, S 7.7%. M. p. at 93–96 °C.

X-ray crystallography

Diffraction data were recorded on a KUMA KM4 diffractometer with graphite-monochromated Mo- K_α radiation using a Sapphire-2 CCD detector (Oxford Diffraction Ltd). The apparatus was equipped with an open flow thermostat (Oxford Cryosystems), which enabled experiments at 120 K. The structures were solved with direct methods and refined with the SHELX98 program package [20] with the full-matrix least-squares refinement based on F^2 .

Basic crystal data, description 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 772024 and 772025 and can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Previously, we described the structures of several mononuclear complexes with different $\text{CoN}_x\text{O}_y\text{S}_z$ and CoN_xS_y cores, most of which were molecular and neutral [21, 22]. As a starting compound for all the syntheses, we use bimetallic $[\text{Co}\{\mu\text{-SSi}(\text{tBuO})_3\}\{\text{SSi}(\text{tBuO})_3\}(\text{NH}_3)_2]$ with

Table 1 Crystal and structure refinement data for complexes **1** and **2**

| Compound | 1 | 2 |
|---|---|--|
| Formula | $\text{C}_{31}\text{H}_{63}\text{NO}_6\text{S}_2\text{Si}_2\text{Co}$ | $\text{C}_{31}\text{H}_{66}\text{N}_2\text{O}_6\text{S}_2\text{Si}_2\text{Co}$ |
| Formula weight | 725.05 | 742.09 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ |
| <i>Unit cell dimensions</i> | | |
| <i>a</i> (Å) | 8.7119(4) | 10.0221(3) |
| <i>b</i> (Å) | 15.1562(7) | 29.4417(9) |
| <i>c</i> (Å) | 16.3029(11) | 16.9752(7) |
| α (°) | 98.930(5) | 90.00 |
| β (°) | 99.469(5) | 123.326(2) |
| γ (°) | 102.953(4) | 90.00 |
| <i>Z</i> | 2 | 4 |
| Volume (Å ³) | 2027.52(19) | 4185.2(3) |
| Calculated density (g cm ⁻³) | 1.188 | 1.178 |
| Absorption coefficient (mm ⁻¹) | 0.622 | 0.605 |
| Crystal size (mm) | 0.21 × 0.12 × 0.05 | 0.2 × 0.1 × 0.05 |
| θ range for data collection (°) | 2.09–25.05 | 2.15–25.05 |
| Reflections collected | 13,858 | 28,608 |
| Independent reflections | 7,180 | 7,392 |
| R_{int} | 0.0357 | 0.0435 |
| Data/restraints/parameters | 7180/0/408 | 7392/0/383 |
| R_1 [$F^2 > 2\sigma(F^2)$] | 0.0438 | 0.0699 |
| R_1 (all data) | 0.0553 | 0.0921 |
| wR_1 (all data) | 0.1258 | 0.2093 |
| GOOF, S | 1.154 | 1.218 |
| Largest difference peak and hole (e Å ⁻³) | 0.601 and -0.686 | 1.285 and -1.397 |

Crystallographic data for the structures **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC 772024 and 772025 (respectively). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk)

Co(II) coordinated by ammonia plus two bridging and two terminal silanethiolato ligands. The addition of a heterocyclic *N*-ligand to a solution of this complex causes breakage of the (Co- μS)₂ ring with simultaneous elimination of ammonia [21, 22].

The currently presented complexes (Scheme 1) have been obtained with dimethylpyridine derivatives that introduce similar steric hindrance on the aromatic ring but with different positioning of the methyl groups. Two equivalents of 2,5-dimethylpyridine added to an *n*-hexane solution of the Co(II) complex gave pink-violet crystals of penta-coordinated $[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(2,5\text{-dimethylpyridine})]$ **1** (Fig. 1)

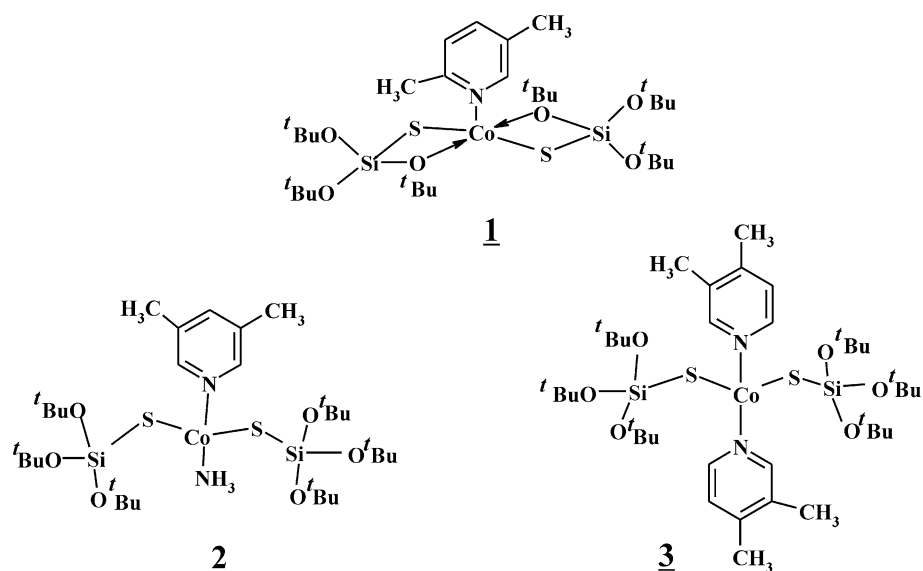
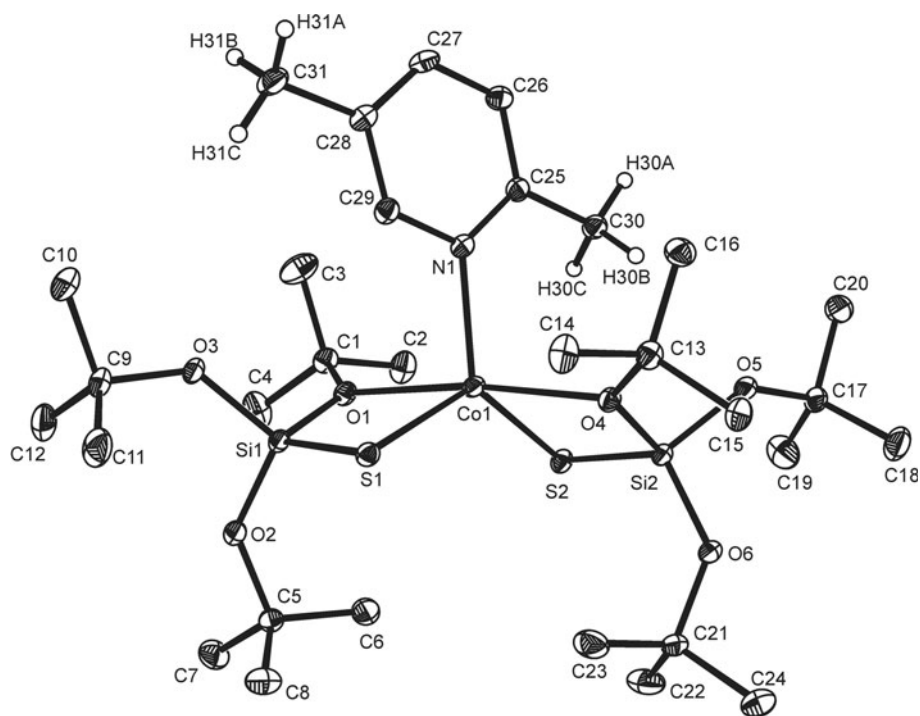
Scheme 1 Obtained complexes**1–3**

Fig. 1 Molecular structure of $\{[\text{Co}\{\text{SSi}(\text{tBuO})_3\}_2]\}$ (2,5-dimethylpyridine) **1** with atom labeling scheme (hydrogen atoms of tBuO groups omitted). Thermal ellipsoids are drawn at 30% probability



which is stable in atmospheric conditions. We did not observe any other products in the reaction mixture, which may suggest that the presence of methyl groups in positions 2 and 5 on the pyridine ring of the amine forces the formation of complex **1** that contains one amine ligand coordinated to the metal.

The result is different when 3,5-dimethylpyridine is used in the synthesis. First of all, an excess of the amine is necessary to obtain the blue crystals of tetrahedral $[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(3,5\text{-dimethylpyridine})(\text{NH}_3)]$ **2**. This complex is coordinated by four ligands: two silanethiolates, one pyridine and one ammonia, giving a CoN_2S_2 kernel to

the complex. Previously, we have obtained a similar compound with 2-methylpyridine [23], which was however significantly less stable than **2**. We have also published the penta-coordinated $[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(3,5\text{-dimethylpyridine})]$ [21], which is a close analog of (3,5-dimethylpyridine)bis(tri-*tert*-butoxysilanethiolato) Zn(II) and Cd(II) [24, 25]. However, the Co(II) complex was obtained in the synthesis with the solution of 2,4,6-trimethylpyridine, in which 3,5-dimethylpyridine was present as a contaminant [21]. We did not obtain this complex in the direct synthesis of the amine with $[\text{Co}\{\mu\text{-SSi}(\text{tBuO})_3\}\{\text{SSi}(\text{tBuO})_3\}(\text{NH}_3)]_2$ in *n*-hexane.

The above results prompted us to explore the synthesis with dimethylpyridine, with the methyl groups located in positions of 3 and 4; the basicity of 3,4-dimethylpyridine ($pK_b = 7.54$) is very similar to that of 3,5-dimethylpyridine ($pK_b = 7.85$). This synthesis also leads to a tetrahedral product, namely $[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(3,4\text{-dimethylpyridine})_2]$ **3**; however, this time Co(II) is coordinated by two silanethiolate residues and two dimethylpyridine ligands. Complex **3** is very soluble in different solvents and precipitates as a blue hair-like forms, and up to now we have

not received any crystals of this compound, despite the use of a variety of crystallization methods. Meanwhile, the composition of **3** was determined by elemental and spectral analysis in the solid state and in solution.

The results obtained, together with the comparison with previous results [21–23], strongly suggest that the steric hindrance exerted by the methyl groups on pyridine has the main influence on the products formation.

Crystal structures

The structures of complexes **1** and **2** with atom labeling schemes and crystal packing are illustrated in Figs. 1, 2, 3 and 4, and selected bonds and angles are listed in Tables 2 and 3.

Complex **1** consists of discrete molecules and crystallizes in space group P-1 with two molecules in a unit cell (Figs. 1 and 2). The central Co(II) atom is coordinated by two S atoms and two O atoms derived from silanethiolate residues and one N atom of 2,5-dimethylpyridine. The geometry of the complex can be described as distorted trigonal bipyramidal with basal plane S1, S2 and N1 and Co1 lying in this plane. The Co1–O1 and Co1–O4 distances (2.3548(16) and 2.3145(15) Å, respectively) distinctly exceed the sum of covalent radii for Co and O, which is equal to 1.89 Å, but are nevertheless shorter than those found in similar metal silanethiolates with methyl and dimethyl pyridine derivatives. The S1–Co1–S2 angle is noticeably one of the narrowest angles among tri-*tert*-butoxysilanethiolate complexes with O,S-chelating bonds of silanethiolate residues [21, 22].

The overall coordination pattern is typical for penta-coordinated Co(II), Mn(II), Zn(II) or Cd(II) tri-*tert*-

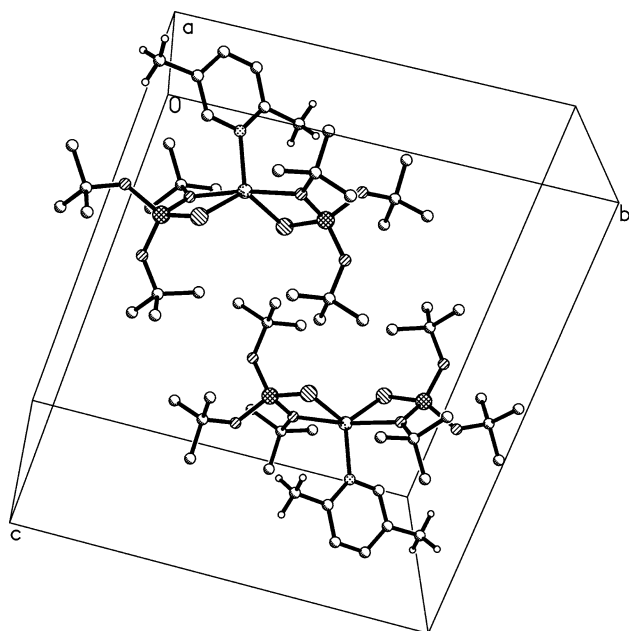
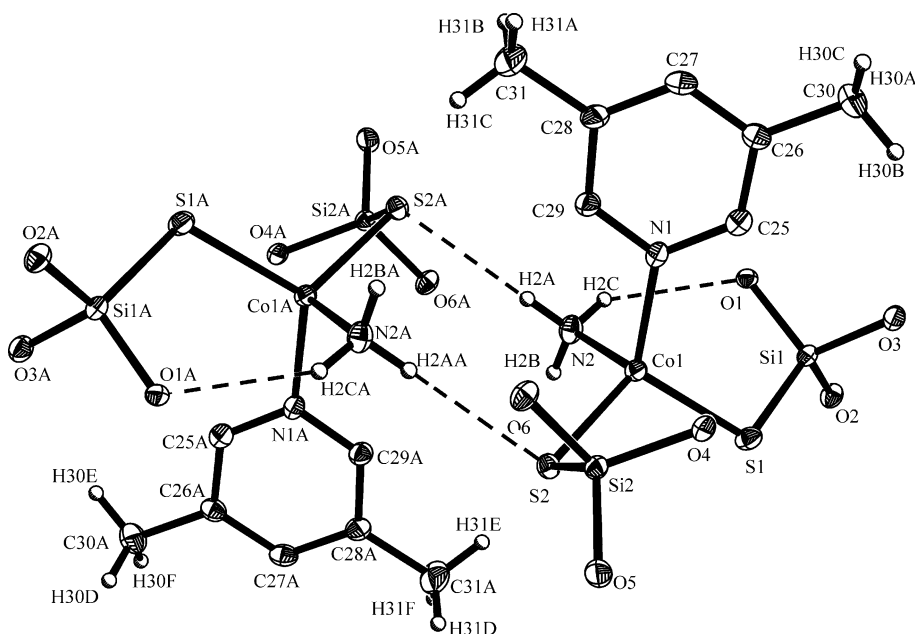


Fig. 2 Crystal packing of **1**. All hydrogen atoms of aromatic ring have been omitted for clarity

Fig. 3 Two molecules of $[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(3,5\text{-dimethylpyridine})(\text{NH}_3)]$ **2** with atom labeling and hydrogen bonds scheme. All *t*Bu groups and hydrogen atoms of aromatic ring are omitted for clarity. Thermal ellipsoids are drawn at 30% probability



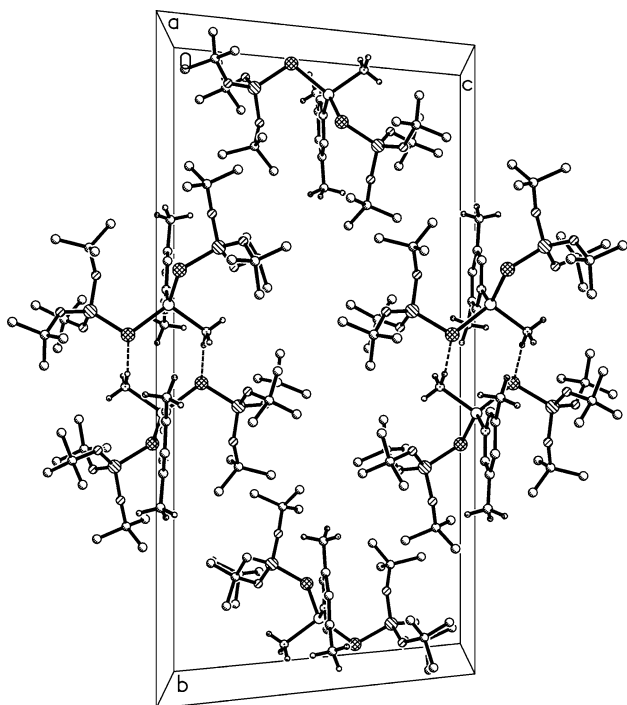


Fig. 4 Crystal packing of **2**

butoxysilanethiolates with pyridines [6, 21, 22, 24, 25], where metal–oxygen distances are longer than the typical covalent bonds. Therefore, considering these observations, we think that the formation of such interactions in silanethiolate complexes is forced by the spatial arrangement of the bulky tert-butoxy groups.

Complex **2** crystallizes in space group $P2_1/c$ with four molecules in a unit cell (Fig. 4). The Co(II) atom is coordinated by two S atoms from the silanethiolate ligands and two N atoms from different ligands, namely ammonia and 3,5-dimethylpyridine. This gives the complex with a tetrahedral structure with CoN_2S_2 core (Fig. 3). Additionally, each ammonia ligand is engaged in two hydrogen bonds: one intermolecular $\text{N}\cdots\text{H}\cdots\text{S}$ of the silanethiolate residue and one intramolecular $\text{N}\cdots\text{H}\cdots\text{O}$ of the tert-butoxy group. These additional interactions enable the formation of two hydrogen-bonded dimers in a unit cell, with the pyridine rings lying in the same plane, approached in a head to tail mode (Fig. 4). In comparison, the congruent complex $[\text{Co}\{\text{SSi}(\text{O}^t\text{Bu})_3\}_2(2\text{-methylpyridine})(\text{NH}_3)]$ contains two intramolecular $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds (distances 3.041(6) and 3.092(6) Å) [23]. The remaining bond lengths and angles in complex **2** are comparable to these found in other Co(II) tri-tert-butoxysilanethiolates.

Spectral analysis

The structures of complexes **1–3** were confirmed with vibrational spectra recorded in the solid state in the range

Table 2 Selected bond lengths (Å) and angles (°) in complexes **1** and **2**

| | 1 | 2 |
|---------------------|------------|------------|
| <i>Bond lengths</i> | | |
| Co(1)–N(1) | 2.088(2) | 2.038(5) |
| Co(1)–N(2) | – | 2.061(5) |
| Co(1)–S(1) | 2.3076(6) | 2.2753(16) |
| Co(1)–S(2) | 2.2894(7) | 2.2966(15) |
| Co(1)–O(1) | 2.3548(16) | – |
| Co(1)–O(4) | 2.3145(15) | – |
| Si(1)–S(1) | 2.0837(8) | 2.069(2) |
| Si(2)–S(2) | 2.0768(8) | 2.087(2) |
| Si(1)–O(1) | 1.6630(17) | 1.642(4) |
| Si(1)–O(2) | 1.6281(17) | 1.632(4) |
| Si(1)–O(3) | 1.6377(17) | 1.630(4) |
| Si(2)–O(4) | 1.6729(17) | 1.631(4) |
| Si(2)–O(5) | 1.6348(17) | 1.623(4) |
| Si(2)–O(6) | 1.6259(17) | 1.635(4) |
| <i>Bond angles</i> | | |
| N(1)–Co(1)–N(2) | – | 99.63(19) |
| N(1)–Co(1)–S(1) | 110.53(6) | 117.90(14) |
| N(2)–Co(1)–S(1) | – | 105.48(14) |
| N(1)–Co(1)–S(2) | 124.14(6) | 113.89(13) |
| N(2)–Co(1)–S(2) | – | 108.38(15) |
| S(2)–Co(1)–S(1) | 125.16(2) | 110.24(6) |
| Si(1)–S(1)–Co(1) | 86.14(3) | 107.56(7) |
| Si(2)–S(2)–Co(1) | 85.39(3) | 104.28(7) |
| S1–Co1–O1 | 77.28(4) | – |
| S2–Co1–O1 | 78.50(4) | – |
| O4–Co1–O1 | 172.78(6) | – |

Table 3 Hydrogen bonds parameters for **2**

| D–H | D–H [Å] | H \cdots A [Å] | D \cdots A [Å] | \angle DHA [°] |
|--------------------|---------|------------------|------------------|------------------|
| N2–H2A \cdots S2 | 0.91 | 2.60 | 3.509(5) | 174.2 |
| N2–H2C \cdots O1 | 0.91 | 2.41 | 3.125(6) | 135.3 |

of 3,500–700 cm^{-1} as presented in Figs. 5 and 6. In metal silanethiolates, where oxygen from the $\text{Si–O}^t\text{Bu}$ ligand interacts with the metal center, we can observe a broad band at about 980 cm^{-1} , as seen in the spectrum of complex **1** (Fig. 5) [22]. This intensity is absent in the spectra of tetrahedral complexes **2** and **3**, and only the strong asymmetric ν (Si–O–C) appears at about 1,010 cm^{-1} (Fig. 5). In contradistinction to complexes **1** and **3**, complex **2** shows additional sharp bands in the region 3,400–3,100 cm^{-1} , ascribed as the antisymmetric and symmetric NH_3 stretching vibrations, as shown in Fig. 6 [26].

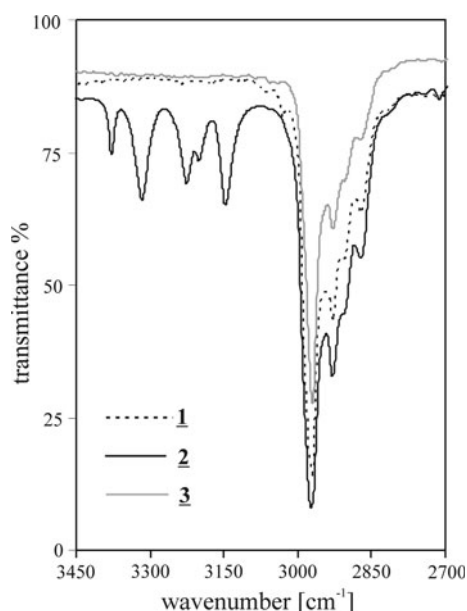


Fig. 5 Solid-state FT-IR spectra of complexes **1–3** in the range 3,400–3,100 cm⁻¹

During the preparation of the *n*-hexane solutions for spectral measurements, we noticed that in the case of dilute solutions, their blue color changes and some indefinite precipitate appears. Therefore, we performed the UV–Vis analysis in order to determine the composition of the complexes in the solutions with diverse concentrations. The results are presented in Fig. 7.

Normally, Co(II) tri-*tert*-butoxysilanethiolates with additional aromatic *N*-ligands show an absorption band at about 270 nm, arising from N → Co LMCT, and a second band at about 350 nm, attributed to S → Co charge transfer transition of the terminal sulfur (S_t) of the silanethiolato residues [22, 27, 28]. Co(II) complexes also show specific d–d transitions in the visible region:

Fig. 6 Solid-state FT-IR spectra of complexes **1–3** in the range 1,700–700 cm⁻¹

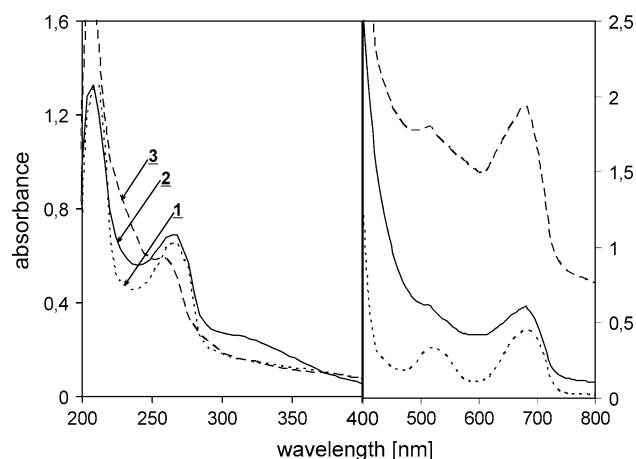
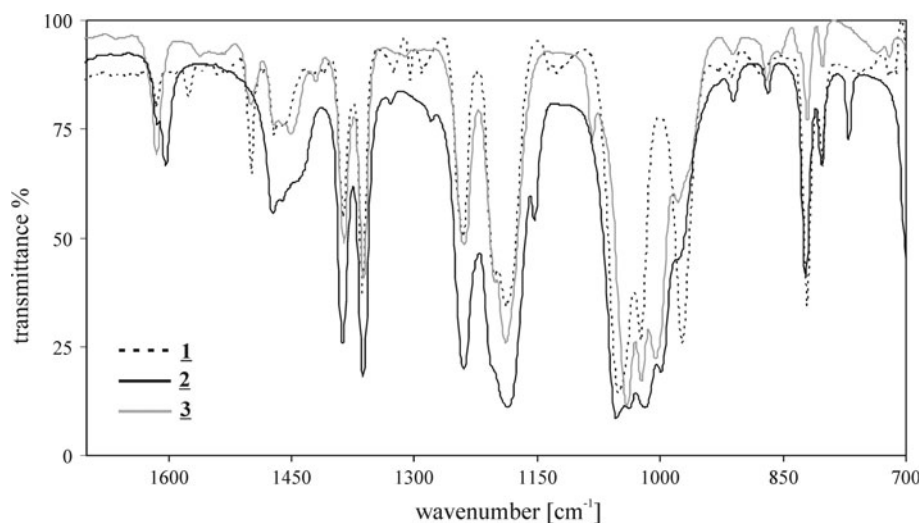


Fig. 7 Electronic spectrum in *n*-hexane solution of complexes **1–3**. Concentration of the solutions: 0.00012 M (UV) and 0.005 M (Vis) **1**; 0.00056 M (UV) and 0.0078 M (Vis) **2**; 0.00012 M (UV) and 0.012 M (Vis) **3**

penta-coordinated complexes show two broad bands at about 520 and 680 nm, whereas three bands in the range of 520–720 nm are characteristic for the ⁴A₂ → ⁴T₁(P) d–d transitions of high-spin pseudotetrahedral compounds [15, 23, 27, 28].

The spectra of complexes **1–3** differ from the spectra of other cobalt(II) silanethiolates with *N*-ligands and in the LMCT region contain only the N → Co LMCT absorption band, shifted insignificantly (264 nm for **2**, 256 nm for **3**) with a visible shoulder. The S_t → Co band is present in the spectrum of complex **2**, but very weak, whereas in the case of complexes **1** and **3**, there is a definite lack of this band. It suggests that in dilute solutions, these complexes dissociate and the number of the silanethiolate ligands on the cobalt atom decreases rapidly.

Changes are also observed in the visible region. The diluted solutions of complexes **1–3** show no absorption

bands in this region. The spectra presented in Fig. 7 are obtained only for concentrated solutions, and only the spectrum of complex **1** contains separated bands, similar to those of penta-coordinated complexes, while the spectra of complexes **2** and **3** reveal some bands, which are not symmetric. These suggest that the examined solutions contain mixtures of the compounds, where Co(II) is four- and five-coordinated, respectively.

Conclusions

Three cobalt(II) tri-*tert*-butoxysilanethiolates with additional dimethylpyridines have been synthesized. The crystal structures have been determined for two of them. The spectral analysis using UV–Vis and IR shows the relative stability of the complexes in the solid state but their instability in dilute solutions. We suppose that the presence of hydrogen bonds stabilizes the structures in the crystals.

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