APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 517–524 **Materials, Nanomaterials and Synthesis** **AOC**
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.332

Cobalt(II) tri-*tert*-butoxysilanethiolates: in search of models for catalytic metal site of liver alcohol dehydrogenase[†,‡]

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Received 12 December 2001; Accepted 17 May 2002

The reaction of dimeric $[Co\{SSi(O^tBu)_3\}_2(NH_3)]_2$ (1) with 2-picoline at 0 °C leads to the formation of a thiolate complex $[Co\{SSi(O^tBu)_3\}_2(NH_3)(2\text{-Pic})]$ (3), with two different nitrogen ligands in the cobalt(II) coordination sphere. Dissolution of 1 in acetonitrile gives one cobalt(II) thiolate complex with two ammine ligands bonded to metal: $[Co\{SSi(O^tBu)_3\}_2(NH_3)_2]\cdot MeCN$ (4). A second, unique, aqua-ligated cobalt(II) thiolate — $[Co\{SSi(O^tBu)_3\}_3(H_2O)]^- \ {}^+HNEt_3$ (5) — forms when $CoCl_2$ reacts with an excess of $(^tBuO)_3SiSH$ in the presence of triethylamine in water. The structures of 3, 4 and 5 were determined by X-ray structure methods, revealing a distorted tetrahedral arrangement of ligands around cobalt. Under normal conditions, all three complexes are unstable. 3 loses ammonia to give stable $[Co\{SSi(O^tBu)_3\}_2(2\text{-Pic})]$ (2). A reverse reaction is also possible. Moreover, 2 is able to capture water, and there is spectral evidence that a complex $[Co\{SSi(O^tBu)_3\}_3(H_2O)(2\text{-Pic})]$ with a $CoNOS_2$ core, mimicking the cobalt-substituted liver alcohol dehyrogenase active site, is formed in solution. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: complexes; cobalt; silanethiolate; thiolate; ammine ligand; aqua ligand; structure; alcohol dehydrogenase

INTRODUCTION

Alcohol dehydrogenases are zinc enzymes that catalyze the reversible dehydrogenation of alcohols to aldehydes and ketones, using the $NADH/NAD^+$ system as a coenzyme:

$$R^1CH(OH)R^2 + NAD^+ \rightleftharpoons R^1COR^2 + NADH + H^+ \qquad (1)$$

The most thoroughly studied liver alcohol dehydrogenases (LADHs) are dimeric enzymes containing two zinc atoms per subunit: one coordinated to four cysteine residues (ZnS_4 core), the second coordinated to two cysteines, one histidine and a water molecule in the resting enzyme. The last site is essential for catalytic activity.[1] In reacting, enzyme water is replaced by an alcohol substrate that undergoes facile deprotonation to the Zinc-bound alkoxide. Hydride transfer between alkoxide α-carbon and NAD^+ interconverts alkoxide and aldehyde or ketone moieties.[2]

Syntheses of complexes reproducing the immediate zinc environment in the LADH active site, therefore, have to focus on neutral monometallic zinc thiolates with $ZnNOS_2$ cores and O-ligands such as water, alcohol, or aldehyde. Thiolate ligands with great steric requirements and/or low basicity were used[3] in order to overcome a common tendency of sulfur to bridge metal centers. This, as well as stabilization of the complexes by *N,O*-chelation, led to the first, and to our knowledge so far the only, structurally characterized $ZnNOS_2$ species (Scheme 1, A–D), reported in 1999 by Vahrenkamp and coworkers.[4]

Unfortunately, the only known $ZnNOS_2$-type complex where a water molecule enters the zinc coordination sphere has an ionic structure[5] (Scheme 1, E).

For many years we have been interested in the chemistry of compounds containing Si—S bonds, and also metal complexes with thiolate ligands derived from trialkoxysilanethiols $(RO)_3SiSH$ (see Ref. 6 and previous papers in the series). Generally, all silanethiols are susceptible to hydrolysis with evolution of hydrogen sulfide (H_2S), but tri-*tert*-butoxysilanethiol $(^tBuO)_3SiSH$[7] is hydrolytically stable.[8] This proved to be very useful as a source of a thiolate ligand,

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[†] This paper is based on work presented at the XIVth FECHEM Conference on Organometallic Chemistry held at Gdansk, Poland, 2–7 September 2001.

[‡] Contribution to the chemistry of silicon–sulfur compounds no. 77. For part no. 76, See Becker *et al.* 2001. Z. Anorg. Allg. Chem. **627**: 280.

Contract/grant sponsor: Polish State Committee of Scientific Research; Contract/grant number: 3 T09A 136 16; Contract/grant number: 7 T09A 115 21.

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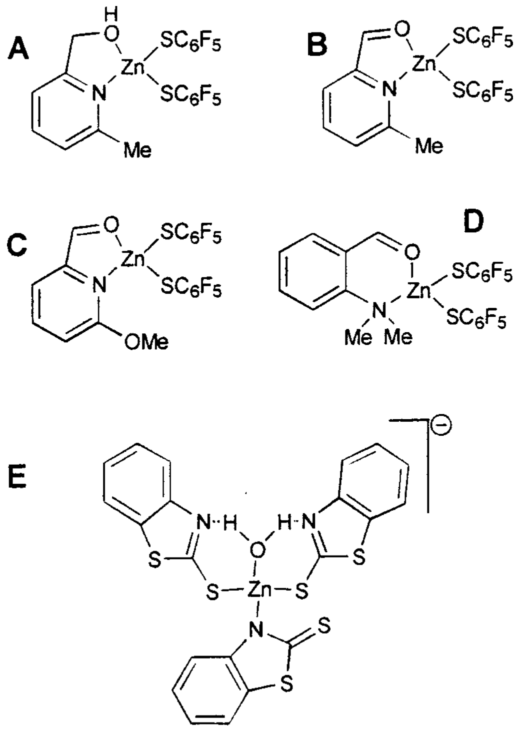

Scheme 1.

leading to many molecular complexes of new, frequently unknown types, including those for zinc. One of these is the first neutral bimetallic zinc silanethiolate [{(^{t}BuO)$_3$SiS}(H$_2$O)$_2$Zn{μ-SSi(O^{t}Bu)$_3$}Zn(acac){SSi(O^{t}Bu)$_3$}] with one zinc atom coordinated by two water molecules and the other by acetylacetonate (ZnO$_2$S$_2$ cores).[9] Three other silanethiolates contain nitrogen ligands: [Zn{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)$_2$]·MeCN and [Zn{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)L] where L = 2-picoline or 2,4-lutidine (ZnN$_2$S$_2$ core).[6] The above compounds turned our attention to the preparation of complexes able to mimic the immediate environment of zinc in the LADH active site. What is more, we intended to prepare complexes with zinc coordinated by four independent ligands. We found this idea particularly appealing when we prepared and structurally characterized some stable cobalt(II) complexes of the overall formula [Co{SSi(O^{t}Bu)$_3$}$_2$L], where L = pyridine and its methyl derivatives (CoNS$_2$ core).[10] With apparently three-coordinated cobalt(II) they seemed to be ideal candidates for the incorporation of a fourth ligand, *e.g.* with oxygen as a donor atom. Since the coordination chemistry of cobalt(II) and zinc(II) is similar, and it is known that cobalt(II)-substituted LADH retains 70% of its enzymatic activity,[11] we decided to focus our attention on cobalt(II) complexes. This paper describes the primary results of our investigations.

RESULTS AND DISCUSSION

The first stage of our investigations was directed toward preparation and characterization of a cobalt(II) complex with tri-*tert*-butoxysilanethiolate, a heterocyclic nitrogen base and ammonia as ligands. In a previous paper we proposed the formation of such a complex in a reaction of a bimetallic, ammonia-ligated cobalt(II) silanethiolate [Co{μ-SSi(O^{t}Bu)$_3$}{SSi(O^{t}Bu)$_3$}(NH$_3$)]$_2$ (**1**)[12] with 2-picoline (1:2 molar ratio) in hexane at room temperature, but the blue crystalline product was unstable; during storage at room temperature or during attempted recrystallization it quickly decomposed to the known[10] pink–violet [Co{SSi(O^{t}Bu)$_3$}$_2$(2-Pic)] (**2**). Now we allowed the same reagents to react at −5 °C. After 2 weeks we managed to isolate crystals of sufficient quality for X-ray measurements and enough stable to withstand *ca* 2 weeks of constant X-ray irradiation at −50 °C. Finally, the solved structure revealed a monometallic complex [Co{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)(2-Pic)] (**3**) with tetrahedrally coordinated cobalt(II), as shown in Fig. 1. A detailed description is given below.

It is worth noting that **3** is isomorphous with the related zinc complex [Zn{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)(2-Pic)],[6] but the latter is completely stable and may be stored unchanged for months. At room temperature, elimination of ammonia from **3** with the formation of apparently more stable **2** takes a few hours. The reaction is reversible (R = SSi{O^{t}Bu}$_3$) (Scheme 2), and when solid pink–violet **2** is subjected to an ammonia atmosphere its color quickly changes to blue. The process may be more conveniently followed spectroscopically. An electronic spectrum (400–800 nm) registered for **2** dissolved in isopropanol changes to the spectrum of **3** after simple addition of a small drop of aqueous ammonia.

3 is the first labile ammine-ligated cobalt silanethiolate. Two others, bimetallic **1** and especially the ionic cobalt(III) complex [Co{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)$_4$]$^+$ $^-$SSi(O^{t}Bu)$_3$, are completely stable.[12] The crystals of another labile compound, with two ammine ligands bonded to cobalt(II), *viz.* [Co{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)$_2$]·MeCN (**4**; see Figs 2 and 3) formed rather unexpectedly when we simply dissolved **1** in acetonitrile and left the solution undisturbed at 0 °C.

How **4** was formed remains unclear, but an explanation must take into account the facile transfer of one ammonia molecule between the two cobalt(II) centers, either within the bimetallic structure of **1** or after the rupture of its central Co$_2$(μ-S)$_2$ ring. **4** is even less stable than **3** and can be stored only at temperatures below 0 °C. Its molecular structure was determined by X-ray methods (for details see below).

We would like to point out that **4** is the first example of a cobalt(II) thiolate complex with two ammine ligands bonded to the same metal center. It seems that complexes with an overall formula (RS)$_2$M(NH$_3$)$_2$, where M is any metal and RS represents any thiolate-like ligand, are extremely rare. The only one was reported by us recently: it is a zinc derivative [Zn{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)$_2$]·MeCN, isomorphous with **4**.[6] Although the complexes were obtained by different methods, both captured the acetonitrile. Only after their molecular structures were solved did the role of the solvent become evident.

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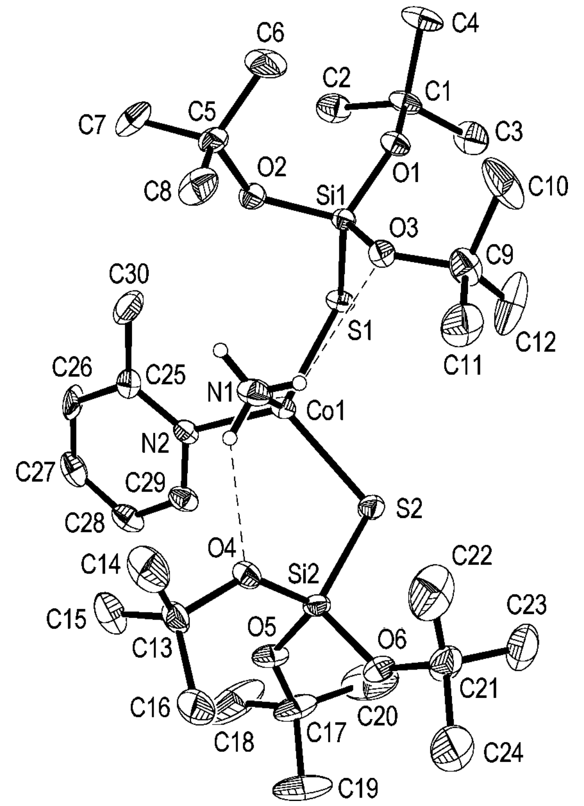


Figure 1. Molecular structure of $[Co\{SSi(O^tBu)_3\}_2(NH_3)(2\text{-Pic})]$ (**3**) with atom labeling scheme. Hydrogen atoms (except for NH_3) are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

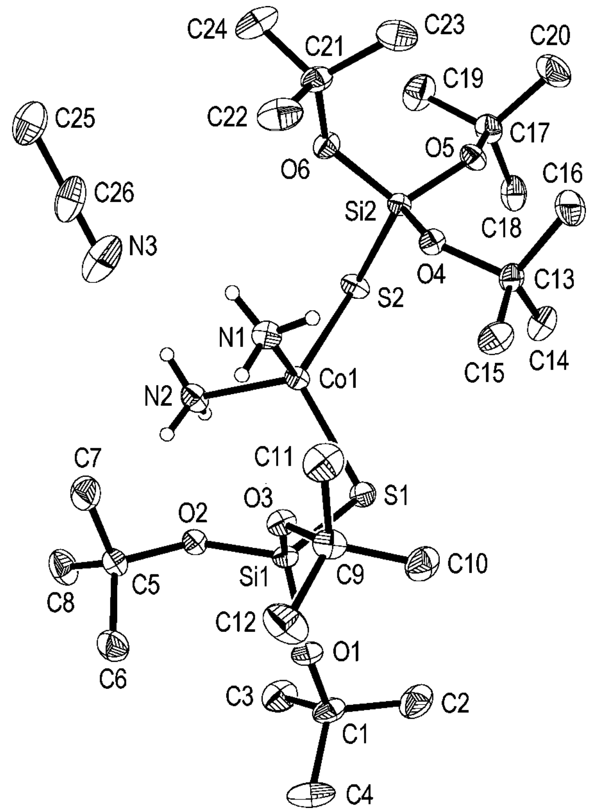
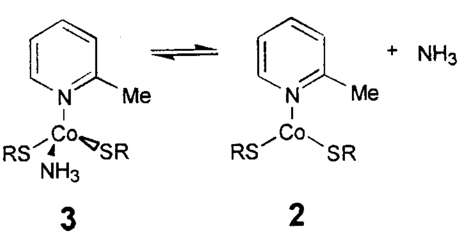


Figure 2. Molecular structure of $[Co\{SSi(O^tBu)_3\}_2(NH_3)_2]\cdot MeCN$ (**4**) with atom labeling scheme. Hydrogen atoms (except for NH_3) are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.

It is remarkable that silanethiolates **1**, **3** and **4** are so far the only known ammine-ligated cobalt thiolates characterized structurally. This, we regard, is a good indication of the usefulness of the tri-*tert*-butoxysilanethiolate ligand, which is apparently able to stabilize complexes hitherto little accessible.

The successful preparation of $[Co\{SSi(O^tBu)_3\}_2(NH_3)(2\text{-Pic})]$ (**3**) prompted us to look for a method of preparation of a closely related complex, but containing water instead of ammonia - $[Co\{SSi(O^tBu)_3\}_2(H_2O)(2\text{-Pic})]$, *i.e.* one having the same $MNOS_2$ core as found in the LADH-active site. Two simple procedures were envisaged:

1. preparation of an aqua-ligated cobalt(II) silanethiolate and its further reaction with a heterocyclic base, *e.g.* 2-picoline;
2. insertion of water into known $[Co\{SSi(O^tBu)_3\}_2(2\text{-Pic})]$ (**2**), *i.e.* the transformation of a three- to a four-coordinated cobalt(II) complex. Both procedures were tested.



Scheme 2.

We found previously[12] that ammine-ligated bimetallic cobalt(II) complex **1** can be easily prepared by a simple reaction of neat tri-*tert*-butoxysilanethiol with $CoCl_2$ dissolved in aqueous ammonia:

$$2CoCl_2 + 6NH_3 + 4(^tBuO)_3SiSH = \underset{(\mathbf{1})}{[Co\{\mu\text{-}SSi(O^tBu)_3\}\{SSi(O^tBu)_3\}(NH_3)]_2} + 4NH_4Cl \quad (2)$$

Triethylamine only very rarely serves as a ligand in transition-metal complexes. We thought, therefore, that the reaction of $(^tBuO)_3SiSH$ with $CoCl_2$ in water as a solvent in the presence of an excess of triethylamine as a hydrogen chloride acceptor may lead to a related aqua-ligated cobalt(II) silanethiolate complex. Indeed, the reaction pro-

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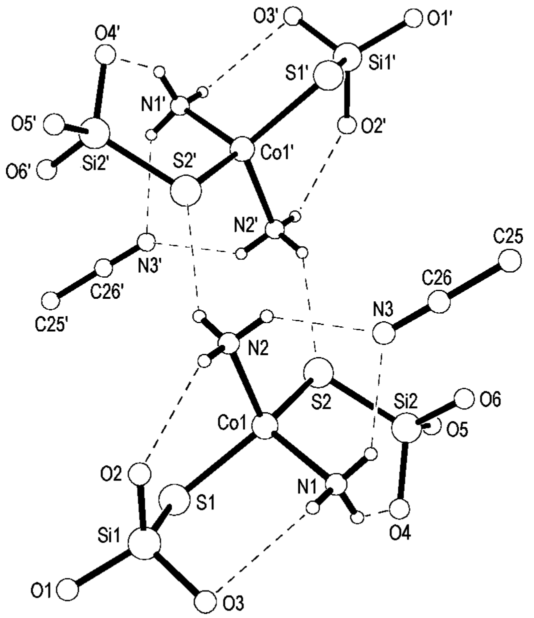

Figure 3. Hydrogen bonds in **4**. All ^{t}Bu groups are omitted.

ceeded smoothly and we obtained the blue product **5**, which is very soluble in common organic solvents, except acetonitrile. It was not stable, and crystals stored at room temperature decomposed within 2 days, giving a green–gray powder that was not analyzed further. A UV spectrum of **5** (Fig. 5A) suggested tetrahedrally coordinated cobalt. Elemental analysis and IR data pointed to the presence of silanethiolate, water, and unexpectedly, triethylamine. Finally, the molecular structure of **5** was solved by X-ray measurements and the complex identified as ionic $[Co\{SSi(O^tBu)_3\}_3(H_2O)]^-$ $^+NHEt_3$, with cation and anion held together by an N—H···S hydrogen bond (Fig. 4). A detailed description of the structure is given below.

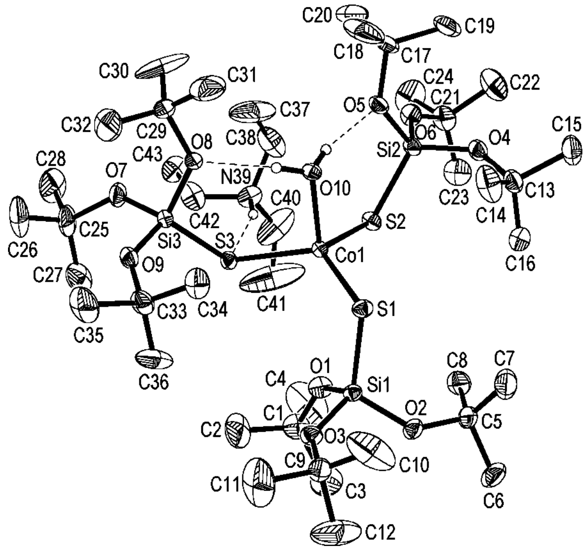

Figure 4. Molecular structure of $[Co\{SSi(O^tBu)_3\}_3(H_2O)]^{-+}NHEt_3$ (**5**) with atom labeling scheme. Hydrogen atoms of CH bonds are omitted for clarity. Thermal ellipsoids are drawn at 20% probability.

When we added 2-picoline to the solution of **5** in hexane, only known $[Co\{SSi(O^tBu)_3\}_2(2\text{-}Pic)]$ (**2**) was isolated. The same complex resulted when a solution of **5** in hexane was exposed to 2-picoline vapors. With pyridine, we observed two steps in the reaction: initial formation of $[Co\{SSi(O^tBu)_2(Py)]$, followed by the formation of $[Co\{SSi(O^tBu)_2(Py)_2]$, both compounds described by us previously.[10] We expected that probably weakly bonded water may be removed from **5**, but a facile elimination of one of the silanethiolate ligands, even from the negatively charged complex, was not so obvious. Numerous stable ionic cobalt(II) thiolates have been obtained and characterized structurally, some of them with such bulky thiolate ligands as $2,3,5,6\text{-}Me_4C_6HS—$,[13] $2,4,6\text{-}{}^iPr_3C_6H_2S—$,[14] or $2\text{-}PhC_6H_4S—$.[15]

When we left the hexane solution of **5** in an ammonia atmosphere, instead of an expected neutral cobalt(III) silanethiolate $[Co\{SSi(O^tBu)_3\}_3(NH_3)_3]$, the ionic complex $[Co\{SSi(O^tBu)_3\}_2(NH_3)_4]^+$ $^-SSi(O^tBu)_3$ was formed almost quantitatively.[12]

Unfortunately, the above results showed clearly that $[Co\{SSi(O^tBu)_3\}_3(H_2O)]^-$ $^+NHEt_3$ (**5**) cannot serve as substrate for the attempted preparation of LADH-active site models. During several experiments, we observed that solutions of pink–violet **2** in polar solvents, such as lower alcohols, THF, or diethyl ether, are sometimes blue, although solutions of the same complex in hexane or benzene are violet. We realized that the change of color was only observed for **2** dissolved in those polar solvents that had not been dried, and so contained some water. Below, we summarize the results obtained from UV–VIS spectral measurements (visible region 400–800 nm). For a more elaborate discussion of the electronic spectra of silanethiolates with three- and four-coordinated cobalt(II), see Ref. 10.

Regarding Fig. 5, we note the following features. Figure 5A shows spectra of **2**, **3**, and **5** registered in hexane. The differences observed for silanethiolates with three- (**2**) and four-coordinated cobalt(II) (**3**, **5**) are evident. Figure 5B presents spectra of **2** registered in hexane, anhydrous THF, and anhydrous isopropanol; regardless of the solvent used, the spectra are almost identical. The spectra shown in Fig. 5C were registered for the same samples as in Fig. 5B, but after addition of one small drop of water (*ca* 10 μl *per* 2 ml of the solution) to each sample. Moreover, we give here the spectrum of **2** dissolved in methanol. The result is clear: a band with a maximum at *ca* 525 nm is shifted to longer wavelengths, indicating the change of coordination at cobalt from three to four.

The observations may be rationalized if we admit that **2** reacts with water or methanol to form tetrahedral complexes of the type $[Co\{SSi(O^tBu)_3\}_2(O\text{-ligand})(2\text{-}Pic)]$, *i.e.* complexes

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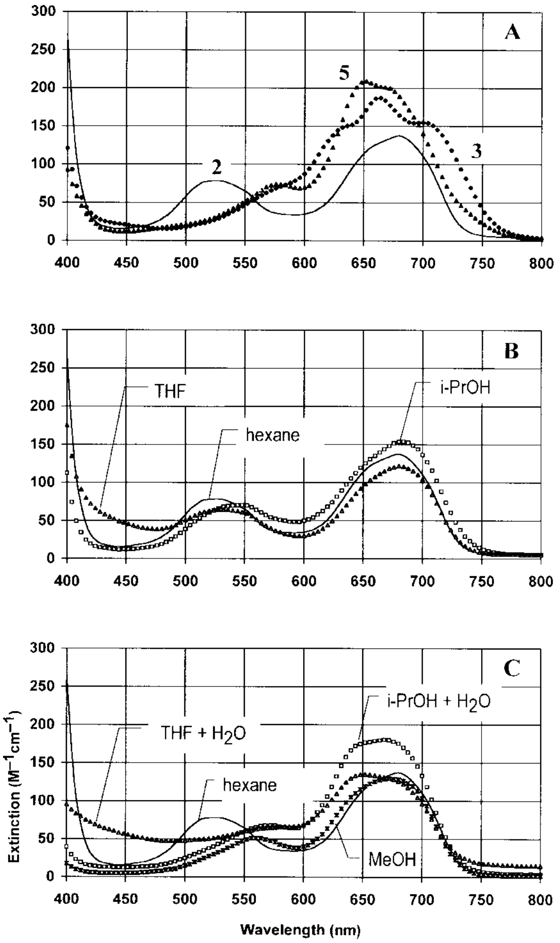

Figure 5. Electronic spectra of selected cobalt(II) silanethiolate complexes: (A) **2**, **3**, and **5** dissolved in hexane; (B) **2** dissolved in hexane, anhydrous THF, and ^{i}PrOH (C) **2** dissolved in hexane, THF + H$_2$O, ^{i}PrOH + H$_2$O, and methanol.

with four independent ligands and the CoNOS$_2$ core we were looking for. If we recall the great steric hindrance caused by two bulky tri-*tert*-butoxysilanethiolate ligands, we can also understand why such a reaction is possible in the presence of water or methanol, but not with isopropanol or THF. Moreover, the reactions of **2** with ammonia (Scheme 2) and with water seem to be reversible. We think that the existence of the tetrahedral [Co{SSi(O^{t}Bu)$_3$}$_2$(H$_2$O)(2-Pic)] complex (at least in solution) seems well justified, and, although our first attempts to isolate it failed, the successful preparation of the related ammine-ligated **3** allows us to hope for a positive final result.

Description of structures

Selected interatomic distances and angles for all three complexes **3, 4**, and **5** are collected in Table 1. The parameters for the hydrogen bonds are given in Table 2.

Table 1. Bond lengths (Å) and angles (°) for **3**, **4**, and **5**

	3	4	5
Co1—N1	2.073(4)	2.0624(18)	
Co1—N2	2.075(4)	2.0507(17)	
Co1—S1	2.3101(15)	2.2981(8)	2.2780(18)
Co1—S2	2.3121(17)	2.3003(9)	2.3180(18)
Co1—S3			2.3293(17)
Co1—O10			2.082(4)
S1—Si1	2.0939(17)	2.0794(9)	2.077(2)
S2—Si2	2.0858(19)	2.0838(11)	2.082(2)
S3—Si3			2.077(2)
C26—N3		1.133(4)	
N1—Co1—N2	109.72(18)	105.00(8)	
N1—Co1—S1	110.72(13)	106.65(5)	
N2—Co1—S1	110.48(12)	109.91(6)	
N1—Co1—S2	104.70(15)	111.79(6)	
N2—Co1—S2	112.62(13)	105.01(5)	
O10—Co1—S1			100.80(13)
O10—Co1—S2			101.29(13)
O10—Co1—S3			100.72(12)
S1—Co1—S2	108.46(6)	117.79(3)	118.54(7)
S1—Co1—S3			123.65(7)
S2—Co1—S3			107.14(7)
Si1—S1—Co1	103.31(6)	100.43(3)	107.72(9)
Si2—S2—Co1	105.96(8)	103.16(4)	114.46(9)
Si3—S3—Co1			114.28(9)
C25—N2—Co1	125.0(4)		
C29—N2—Co1	117.1(3)		
N3—C26—C25		179.5(4)	

$[Co\{SSi(O^tBu)_3\}_2(NH_3)(2\text{-}Pic)]$ (**3**)

The structure of the complex is illustrated in Fig. 1. The molecule of **3** is characterized by a tetrahedral arrangement of the ligands. The distortions from an ideal angle value of 109.5° are smaller than in two other complexes investigated. Not only do the atoms {N1, Co1, S1, Si1}, {S1, Co1, S2, Si2}, and {S2, Co1, N2, C29} lie in almost perfectly planes — the respective torsion angles are 1.97(17)°, 176.86(6)° and 0.0(4)° — but also the 2-picoline plane almost perfectly bisects the N1—Co1—S1 angle. Bond lengths and angles within both silanethiolate ligands are fully comparable. Even for very different N-based ligands both Co—N bonds have the same length. Two hydrogen atoms of the ammine ligand form intramolecular N—H···O hydrogen bonds (depicted as dotted lines). The values of the Co—S, Co—N, S—Si, and Si—O bond lengths are unexceptional and comparable to these found in other cobalt thiolates and silanethiolates (e.g. see, discussions in Refs.[10] and[12]). Moreover, **3** and the related zinc complex [Zn{SSi(O^{t}Bu)$_3$}$_2$(NH$_3$)(2-Pic)][6] are isomorphous, and close inspection of the two structures reveals only small differences.

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Table 2. Hydrogen bonds in **3**, **4**, and **5** with distance H···A $<r(A) + 2.000$ Å and angle ∠DHA $>110°$

	D−H	$d(D-H)^a$	$d(H\cdots A)$	∠DHA	$d(D\cdots A)$	A
3	N1−H1B	0.90	2.34	135.1	3.041(6)	O4
	N1−H1C	0.90	2.55	119.3	3.092(6)	O3
4	N1−H1A	0.90	2.56	135.5	3.261(3)	O3
	N1−H1B	0.90	2.47	132.1	3.149(3)	O4
	N1−H1C	0.90	2.54	140.6	3.285(4)	N3
	N2−H2D	0.90	2.37	136.2	3.088(3)	O2
	N2−H2E	0.90	2.51	137.3	3.230(4)	N3
	N2−H2F	0.90	2.77	144.3	3.539(2)	$S2'^b$
5	O10−H10D	0.85	1.90	166.4	2.735(7)	O8
	O10−H10E	0.85	1.92	168.0	2.761(7)	O5
	N39−H39A	0.90	2.64	141.0	3.388(7)	S3

[a] Fixed during refinement.

[b] Equivalent atoms generated by: $x+2, -y+1, -z$.

$[Co\{SSi(O^tBu)_3\}_2(NH_3)_2]\cdot MeCN$ (**4**)

The structure of the complex is illustrated in Figs 2 and 3. The ligand geometry at the cobalt(II) center is distorted tetrahedral, with the S1−Co1−S2 angle the widest and the N1−Co1−N2 angle the smallest. The bond lengths and angles are rather unexceptional, and they fall within the range observed in other cobalt(II) thiolate complexes, including also those with silanethiolate ligands. A characteristic structural feature of complex **4** is a net of hydrogen bonds within a unit comprised of two molecules of complex and two well-ordered molecules of acetonitrile. All ammine hydrogen atoms are in close contact with appropriate acceptors. We can find here all kinds of possible hydrogen bonds: intramolecular N−H···O, intermolecular N−H···S, and finally N−H···N to the solvent. This probably significantly enhances the overall stability of the complex and makes it accessible. The related zinc complex $[Zn\{SSi(O^tBu)_3\}_2(NH_3)_2]\cdot MeCN$[6] is isomorphous with **4**.

$[Co\{SSi(O^tBu)_3\}_3(H_2O)]^-\ {}^+NHEt_3$ (**5**)

The crystal structure of complex **5** revealed a pair of ions held together by an N−H···S hydrogen bond. Figure 4 gives a view of the complex. In the $[Co\{SSi(O^tBu)_3\}_3(H_2O)]^-$ anion of **5** cobalt(II) is bonded to three silanethiolate ligands through sulfur atoms, and to the oxygen atom of an H_2O molecule. The geometry at the metal center may be regarded as distorted tetrahedral, although S−Co−S angles, especially these involving the S1 atom, are significantly wider than S−Co−O and the S_3O tetrahedron is flattened, with three sulfur atoms forming a base. Two hydrogen atoms from water are engaged in hydrogen bonds to adjacent siloxy oxygen atoms. Despite the anionic nature of the complex, the Co−S bond lengths are comparable to the values observed in other neutral silanethiolates with four-coordinated cobalt(II),[10,12] with the shortest one (Co1−S1) present in the silanethiolate ligand that is not engaged in any secondary interactions. Also the Co1−S1−Si1 bond angle is the smallest one (107.7° compared with 114.5° and 114.2° for the two others). The lengths of all three S−Si bonds are almost identical and by no means unique. The geometry of the $^+HNEt_4$ cation is unexceptional and warrants no further discussion.

Complexes similar to **5** are unknown. The only one that may be quoted here is the ionic zinc thioacetate $[PPh_4][Zn(SC\{O\}Me)_3(H_2O)]$,[16] which has a central $ZnOS_3$ core of the same type as in **5**. Both its Zn−O bond length of 2.084 Å and Zn−S bond lengths of 2.310–2.345 Å are comparable to the appropriate cobalt-based bond lengths found in **5** which makes the central parts of both complexes indeed similar.

EXPERIMENTAL

$[Co\{SSi(O^tBu)_3\}_2(NH_3)]_2$ (**1**)[12] and $[Co\{SSi(O^tBu)_3\}_2(2\text{-}Pic)]$ (**2**)[10] were prepared as described previously. All other reagents were obtained commercially. 2-Picoline was dried with KOH and distilled before use. Solvents were distilled and dried by standard procedures if needed. Electronic spectra were recorded on a Unicam SP300 spectrometer. Elemental analyses were performed on an Elemental Analyser EA 1108 (Carlo Erba Instruments).

$[Co\{SSi(O^tBu)_3\}_2(NH_3)(2\text{-}Pic)]$ (3)

$[Co\{SSi(O^tBu)_3\}_2(NH_3)]_2$ (**1**) (0.255 g, 0.2 mmol) was dissolved in 5 ml of dry *n*-hexane. To the green solution obtained, cooled below 0 °C, 0.037 g (36 µl, 0.4 mmol) of pure 2-picoline was added in one portion. The solution turned blue instantly and was left to stand at −5 °C. After a few weeks well-formed blue crystals separated. These were

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Table 3. Crystal data and structure refinement for **3**, **4**, and **5**

	3	**4**	**5**
Empirical formula	$C_{30}H_{64}CoN_2O_6S_2Si_2$	$C_{26}H_{63}CoN_3O_6S_2Si_2$	$C_{42}H_{99}CoNO_{10}S_3Si_3$
Formula weight	728.06	693.02	1017.60
Temperature (K)	223(2)	200(2)	223(2)
Wavelength (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Crystal system, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic, Cc
Unit cell dimensions			
a (Å)	9.483(2)	9.538(2)	15.868(3)
b (Å)	13.333(3)	13.089(3)	22.999(5)
c (Å)	18.332(4)	16.864(3)	17.725(4)
α (deg)	110.70(3)	81.29(3)	90
β (deg)	100.88(3)	76.32(3)	110.16(3)
γ (deg)	93.59(3)	76.78(3)	90
Volume (Å^3)	2108.0(8)	1980.8(7)	6072(2)
Z, Calculated density (Mg m^{-3})	2, 1.147	2, 1.162	4, 1.113
Absorption coefficient (mm^{-1})	0.599	0.635	0.489
$F(000)$	786	750	2220
Crystal size (mm^3)	0.3 × 0.3 × 0.4	0.4 × 0.5 × 0.6	0.2 × 0.3 × 0.6
θ range for data collection (deg)	1.22 to 29.93	1.61 to 30.52	1.63 to 30.05
Limiting indices	$-12 \leq h \leq 13$, $-17 \leq k \leq 7$, $-25 \leq l \leq 16$	$-13 \leq h \leq 11$, $-18 \leq k \leq 16$, $-23 \leq l \leq 0$	$-21 \leq h \leq 20$, $0 \leq k \leq 32$, $0 \leq l \leq 23$
Reflections collected/unique	10 933/10 296 ($R_{int} = 0.0367$)	9063/8739 ($R_{int} = 0.0404$)	8216/8152 ($R_{int} = 0.3209$)
Completeness to θ_{max} (%)	84.1	72.0	89.2
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10 296/0/389	8739/0/361	8152/221/541
Goodness-of-fit on F^2	1.085	1.039	1.121
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0584$, $wR_2 = 0.1701$	$R_1 = 0.0368$, $wR_2 = 0.1015$	$R_1 = 0.0525$, $wR_2 = 0.1473$
R indices (all data)	$R_1 = 0.2272$, $wR_2 = 0.2655$	$R_1 = 0.0478$, $wR_2 = 0.1087$	$R_1 = 0.1097$, $wR_2 = 0.1706$
Largest diff. peak and hole (eÅ^{-3})	0.816 and −1.609	0.685 and −0.380	0.605 and −0.503

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washed with a small portion of cold *n*-hexane and quickly dried in a stream of argon. M.p. 133–135 °C. Yield: 50%.

Anal. Found: C, 49.97; H, 9.08; N, 3.59; S, 8.85. Calc. for $C_{30}H_{64}CoN_2O_6S_2Si_2$: C, 49.49; H, 8.86; N, 3.85; S, 8.81%.

$[Co\{SSi(O^tBu)_3\}_2(NH_3)_2(CH_3CN)]$ (4)

$[Co\{SSi(O^tBu)_3\}_2(NH_3)]_2$ (**1**) (0.255 g, 0.2 mmol) was dissolved in 3 ml of acetonitrile at room temperature. The green–blue solution obtained was left to stand at 0–5 °C. After 2 weeks, dark-blue crystals were collected and quickly dried in a stream of argon. M.p. 77–78 °C. Yield: 0.085 g, 23%.

Anal. Found: C, 44.84; H, 9.02; N, 5.94; S, 9.20. Calc. for $C_{26}H_{63}CoN_3O_6S_2Si_2$: C, 45.06; H, 9.16; N, 6.06; S, 9.25%.

$[Co\{SSi(O^tBu)_3\}_3(H_2O)][NHEt_3]$ (5)

Triethylamine (20 mmol, 2.8 ml) was added to the cobalt(II) chloride hexahydrate (1.05 mmol, 0.25 g) solution in 50 ml of water. The reaction flask was then closed with a rubber septum and neat tri-*tert*-butoxysilanethiol (12.8 mmol, 3.9 ml) was added dropwise by a syringe to the well-stirred solution. A blue hydrophobic substance was formed immediately. The reaction mixture was then shaken vigorously for *ca* 30 min. The precipitate was collected, washed with cold water, and dried in an air stream for several hours. The dry finely crushed solid was added to 20 ml of *n*-hexane and traces of dark insoluble material removed by filtration. The filtrate was dried with anhydrous magnesium sulfate. Cooling and slow concentration of the solution gave 0.815 g of dark-blue crystals. M.p. 77–78 °C. Yield: 76%.

Anal. Found: C, 49.48; H, 10.0; N, 1.31; S, 9.49. Calc. for $C_{42}H_{99}CoNO_{10}S_3Si_3$: C, 49.57; H, 9.81; N, 1.38; S, 9.45%.

Structure determinations

Diffraction data were recorded on a KUMA KM4 diffractometer with graphite-monochromated Mo K_α radiation. No absorption corrections were applied. The structures were solved with direct methods and refined with the SHELX97 program package[17,18] with the full-matrix least-squares refinement based on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined in geometrically idealized position with isotropic temperature factors 1.2 times the equivalent isotropic temperature factors U_{eq} of their attached atoms (1.5 for CH_3 groups). Crystal data, a description of the diffraction experiment, and details of the structure refinement are given in Table 3.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on quoting the full journal citation and deposition numbers 175422 (**3**), 175423 (**4**), and 175424 (**5**).

REFERENCES

1. Luchinat C and Sola M. Zinc enzymes. In *Encyclopedia of Inorganic Chemistry*, vol. 8, King RB (ed.). John Wiley & Sons Ltd: Chichester, 1994; 4406–4434.
2. Bertini I and Luchinat C. The reaction pathways of zinc enzymes and related biological catalyst. In *Bioinorganic Chemistry*, Bertini I, Gray HB, Lippard SJ, Valentine JS (eds). University Science Books: Mill Valley, CA, USA, 1994; 37–106.
3. Dance IG. *Polyhedron* 1986; **5**: 1037.
4. Müller B, Schneider A, Tesmer M and Vahrenkamp H. *Inorg. Chem.* 1999; **38**: 1900.
5. McCleverty JA, Morrison NJ, Spencer N, Ashworth CC, Bailey NA, Johnson MR, Smith JMA, Tabbiner BA and Taylor CR. *J. Chem. Soc., Dalton Trans.* 1980; 1945.
6. Becker B, Dołęga A, Konitz A, Swinder L and Wojnowski W. *Z. Anorg. Allg. Chem.* 2001; **627**: 280.
7. Piękoś R and Wojnowski W. *Z. Anorg. Allg. Chem.* 1962; **318**: 212.
8. Herman A, Becker B and Wojnowski W. *Z. Anorg. Allg. Chem.* 1979; **450**: 178.
9. Becker B, Dołęga A, Konitz A and Wojnowski W. *Polyhedron* 2001; **20**: 949.
10. Becker B, Zalewska A, Konitz A and Wojnowski W. *Polyhedron* 2001; **20**: 2567.
11. Bertini I, Luchinat C and Viezzoli MS. In *Zinc Enzymes*, Bertini I, Luchinat C, Maret W, Zeppezauer M (eds). Birkhauser: Basel, 1986; 27, (chapter 3).
12. Becker B, Zalewska A, Konitz A and Wojnowski W. *Z. Anorg. Allg. Chem.* 2001; **627**: 271.
13. Koch SA, Fikar R, Millar M and O'Sullivan T. *Inorg. Chem.* 1984; **23**: 121.
14. Ruhlandt-Senge K and Power PP. *J. Chem. Soc., Dalton Trans.* 1993; 649.
15. Silver A, Koch SA and Millar M. *Inorg. Chim. Acta* 1993; **205**: 9.
16. Sampanthar JT, Deivaraj TC, Vittal JJ and Dean PAW. *J. Chem. Soc., Dalton Trans.* 1999; 4419.
17. Sheldrick GM. *Acta Crystallogr. Sect. A* 1990; **46**: 467.
18. Sheldrick GM. SHELX-97. Programs for the solution and the refinement of crystal structures from diffraction data. University of Göttingen, Germany, 1997.

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