Polyhedron 30 (2011) 2400–2405

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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

Łukasz Ponikiewski, Agnieszka Pladzyk *, Wiesław Wojnowski, Barbara Becker

Department of Inorganic Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza Str. 11/12, 80-233 Gdańsk, Poland

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].

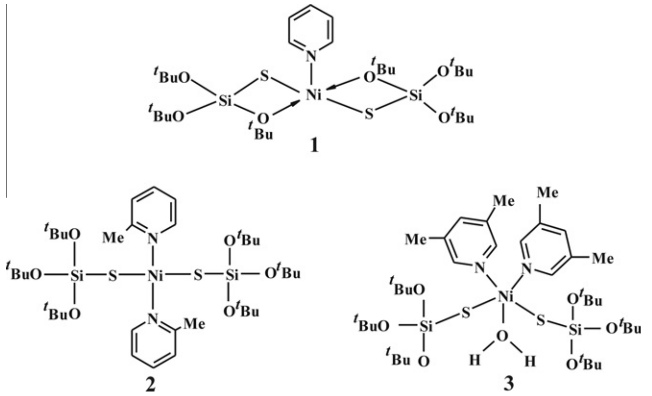
In recent years, our work has been targeted towards biomimetic studies and the prevalent part of these was devoted to zinc thiolates [18]. Now we have turned our attention to nickel complexes with S-thiolate and N-donor ligands that may serve as biomimetic models for the active sites of nickel-containing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

---

* Corresponding author. Tel.: +48 583472329; fax: +48 583472694.
E-mail address: agnieszka.pladzyk@pg.gda.pl (A. Pladzyk).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
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 (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 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 (τ) has been calculated [54,55]. 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 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