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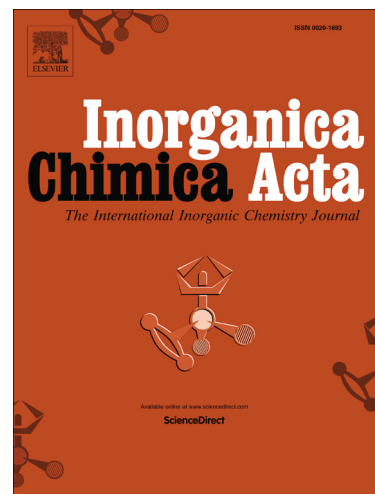
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# Synthesis and molecular structure of a zwitterionic ZnI<sub>2</sub> silanolate

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**Keywords:** metal silanolates; silicon; siloxanes; X-ray crystallography; zinc

**Abstract:** A new representative of hydrolysis-stable zwitterionic ZnHal<sub>2</sub> silanolates (with Hal = I) was obtained by treatment of an aminomethyl-functionalised disiloxane with zinc(II) iodide. The molecular structure was elucidated by X-ray crystallography and NMR spectroscopy.

substituted zinc silanolates were synthesised, directly starting from the corresponding planar-chiral silanols [23], which can be easily provided by enantioselective *ortho*-lithiation of (aminomethyl)ferrocene, a method lately developed in our group [24]. Recently, we also reported on a simplified bio-inspired, metal-free aggregate built by a silanol and an ammonium acetate [25].

The effect of the zinc salt towards the siloxane bond cleavage and the coordination mode within the zinc silanolates formed has not yet been investigated systematically. Herein, we present the synthesis and molecular structure of the first ZnI<sub>2</sub> representative within the class of amino-functionalised zwitterionic ZnHal<sub>2</sub> silanolates. Tetramethyl-1,3-bis(piperidino-methyl)disiloxane (**1**) was chosen as starting compound for the Si–O–Si cleavage with ZnI<sub>2</sub> (Scheme 1). The ZnHal<sub>2</sub> silanolates (with Hal = Cl, Br) as well as a monomeric silanolate species which is coordinated to a [Zn<sub>2</sub>(OAc)<sub>2</sub>(μ-OAc)<sub>2</sub>] moiety (OAc = acetate) were previously reported by our group, also using disiloxane **1** for the cleavage reaction [19,20].

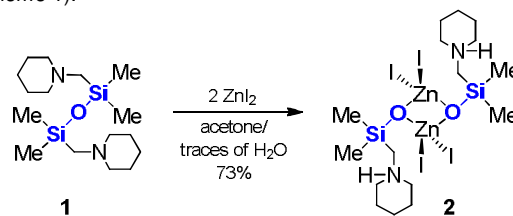
## 1. Introduction

The siloxane bond (Si–O–Si) is the most abundant structural motive in the Earth's crust and can be found in diverse modifications of silica (e.g. quartz) and silicate minerals like aluminosilicates [1,2]. Oxonitridosilicates have gained increased interest in materials science because of their high chemical and thermal stability [3]. Also marine organisms like diatoms and sponges make use of nanostructured silica skeletons by shape-controlled condensation (biomineralisation) of dissolved silicic acid from seawater [4]. Recently, the isolation of monomeric silicon dioxide using a donor-acceptor ligand system was reported [5]. Organo-substituted siloxanes are an industrially important class of polymeric compounds with many applications in our daily life [6]. The development of new synthetic methods for providing silsesquioxanes [7], polysiloxanes [8], and functionalised disiloxanes [9,10] has become an intensively studied area in current silicon research, opening new applications for silicon-based polymers [11]. Siloxy-substituted ZnO aggregates are promising molecular single-source precursors for the preparation of zinc oxide nanoparticles [12,13]. Defined molecular structures composed of metal ions and silanolates are also interesting model systems for mimicking complex silica materials in nature [14]. Since the importance of peptides and polyamines during the silicification process in biological systems is well-documented [15,16], and due to the fact that there is a correlation between silica production and the amount of zinc in seawater [17,18], amino-substituted zinc silanolates are interesting molecular models that may contribute to a better understanding of the biogenesis of silicate structures.

In 2009, we first reported the zinc(II)-mediated cleavage of the Si–O–Si bond in aminomethyl-functionalised disiloxanes under mild conditions in the presence of water, forming zwitterionic hydrolysis-stable zinc silanolates [19,20]. According to DFT calculations, this reaction may also be assisted by interaction of the siloxane oxygen atom with the metal centre [19,21], despite the low basicity of oxygen within the Si–O–Si linkage [22]. Quite recently, also a variety of planar-chiral amino-

## 2. Results and discussion

Treatment of compound **1** with two equivalents zinc(II) iodide in non-dried acetone resulted in a cleavage of the Si–O–Si bond, with the zwitterionic ZnI<sub>2</sub> silanolate **2** being obtained in 73% yield (Scheme 1).



**Scheme 1** Synthesis of the zwitterionic zinc(II) silanolate **2** by selective cleavage of the Si–O–Si bond in disiloxane **1**.

Compound **2** directly crystallised from the reaction mixture in the monoclinic crystal system, space group  $P2_1/n$ , as colourless plates (Figure 1 and Table 1) and could be fully characterised. Analogous to the known lighter ZnHal<sub>2</sub> homologues (Hal = Cl, Br), **2** exists as a dimer with a crystallographic centre of inversion located in the perfectly planar Zn–O–Zn–O' four-membered ring. The zinc atoms are tetra-coordinated by two oxygen and two iodine atoms and show a *pseudo*-tetrahedral coordination sphere with an endocyclic O–Zn–O' angle of 86.05(8)° and an exocyclic I(1)–Zn–I(2) angle of 115.299(14)°. The nitrogen atoms are protonated, which is also indicated by the highfield shift of the <sup>13</sup>C{<sup>1</sup>H} NMR signals of the piperidino-methyl groups (with respect to compound **1**) [19,20], and points

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