Inorganic Polysulfanes $H_2S_n$ with $n > 1$

Ralf Steudel

Institut für Chemie, Sekr. C2, Technische Universität Berlin, 10623 Berlin, Germany
E-mail: steudel@schwefel.chem.tu-berlin.de

Abstract The sulfanes $H_2S_n$ form a long series of homologous chain-like molecules, starting with hydrogen sulfide and running at least up to $H_2S_{35}$. These molecules are the parent compounds of numerous derivatives with either organic or inorganic substituents. In this chapter the preparation, structures, physical and chemical properties as well as the spectra of the sulfanes with $\geq 2$ sulfur atoms are reviewed. In the literature these species are termed either sulfanes, polysulfanes, or hydrogen polysulfides.

Keywords Sulfur hydrides · Molecular structures · Reactivity · Spectra · Acidities · Application

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List of Abbreviations

TMS Tetramethylsilane
XANES X-ray absorption near edge structure

1 Introduction

The rather high bond enthalpy of sulfur-sulfur single bonds as in S₈ (264 kJ mol⁻¹) has the consequence that numerous compounds exist in which sulfur atoms form homoatomic chains, rings or clusters. The sulfanes or hydrogen polysulfides H₂Sₙ are the most basic of these species and all other chain-like sulfur-rich compounds may be considered to be derivatives thereof. For example, the dihalogenosulfanes SₙCl₂ [1], the diorganyl-sulfanes R₂Sₙ [2], the sulfane oxides R₂SₙO [2, 3], and the inorganic polysulfides Sₙ²⁻ [4]. The latter are simply the dianions of the Brønsted acids H₂Sₙ and protonation of these anions is a convenient method to prepare sulfane mixtures. The name sulfane has been created in analogy to the boranes, alkanes, silanes, and phosphanes [5].

Mixtures of polysulfanes H₂Sₙ are easy to make and probably occur even naturally but the pure compounds are relatively unstable and can therefore be prepared only with some experimental skills and observing certain technical precautions. Detailed prescriptions exist how to make di-, tri-, tetra-, and higher sulfanes in gram quantities. However, as longer the sulfur chain grows as more difficult it becomes to obtain pure compounds. In general, all