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Thio-hydroxogermanates: a Novel Type of Mixed Tetrahedral Anions

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Recently, a number of different monomeric and oligomeric thio- and selenoanions of germanium(IV) have been synthesized from aqueous and alcoholic solutions, and most of them were characterized by X-ray structure analyses. Examples for these anions are GeS_4^{4-} [1], $Ge_2S_6^{4-}$ [2], $Ge_2S_7^{6-}$ [3], $Ge_4S_{10}^{4-}$ [4], $Ge_8S_{19}^{6-}$ [5–7], $GeSe_4^{4-}$ [8], $Ge_2Se_6^{4-}$ [9], and $Ge_4Se_{10}^{4-}$ [9]. In spite of several attempts, however, no simple mixed thio-oxoanions of germanium (or tin) could be prepared up to now, either from high-temperature syntheses or from aqueous solutions. This is in contrast to the well-known homologous series of mixed anions $MS_xO_{4-x}^{3-}$ which are formed by the fifth group elements M = P(V), As(V) an Sb(V).

We have now been able to isolate from aqueous solutions the first tetrahedral thio-oxoanions of a main group IV element and report here the first results on the preparation and structures. Dithiodihydroxogermanate $GeS_2(OH)_2^{2-}$ was obtained by reacting stoichiometric quantities of GeS_2 and aqueous NaOH, or GeO_2 and aqueous Na_2S according to $GeS_2 + 2\ OH^- \rightarrow GeS_2(OH)_2^{2-}$, and $GeO_2 + 2S^{2-} \xrightarrow{+2H^+} GeS_2(OH)_2^{2-}$, both reactions representing degradations of the polymeric chalcogenides to the monomeric products by nucleophilic attack of OH^- or S^{2-}. As Raman spectra show, oligomeric thiohydroxogermanates are formed as intermediates. Colourless highly soluble alkali and alkaline earth salts of the $GeS_2(OH)_2^{2-}$ ion are isolated from the solutions by adding a large excess of acetone.

Crystals of $Na_2GeS_2(OH)_2 \cdot 5H_2O$ are orthorhombic, space group Pbcn, with the unit cell constants a = 10.752(2), b = 13.787(2), c = 14.150(2) Å, V = 2097.5 Å^3, Z = 8. According to a single-crystal X-ray analysis (R = 0.032), the crystal structure contains tetrahedral $GeS_2(OH)_2^{2-}$ ions with approximate C_{2v} symmetry of the GeS_2O_2 backbone besides a system of edge-sharing $Na(OH_2)_5(OH)$ octahedra, cations and anions being linked through the OH groups and an extensive O–H···S hydrogen bridge system. In Fig. 1 the $GeS_2(OH)_2^{2-}$ ion is shown with bond lengths and angles.

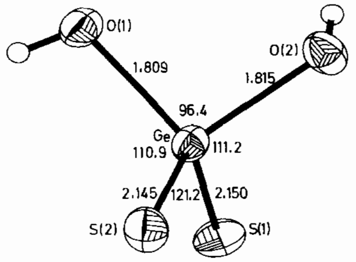

Fig. 1. $GeS_2(OH)_2^{2-}$ ion in the crystal structures of $Na_2GeS_2(OH)_2 \cdot 5H_2O$ with bond lengths (A) and bond angles (°). Standard deviations are 0.001 A for Ge–S, 0.003 A for Ge–O, 0.1° for angles.

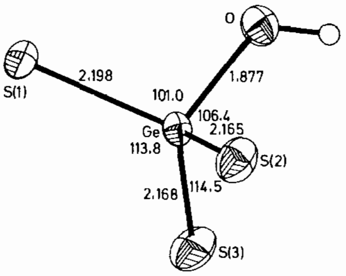

Fig. 2. $GeS_3(OH)^{3-}$ ion in the crystal structure of $Na_3GeS_3(OH) \cdot 8H_2O$ with bond lengths (A) and bond angles. Standard deviations are 0.003 A for Ge–S, 0.007 A for Ge–O, 0.2° for angles.

Trithio-monohydroxogermanate $GeS_3(OH)^{3-}$ was prepared in a similar way as $GeS_2(OH)_2^{2-}$ from solutions of GeS_2 in aqueous mixture of NaOH + Na_2S, the three components taken in a 1:1:1 molar ratio according to the stoichiometric reaction $GeS_2 + S^{2-} + OH^- \rightarrow GeS_3(OH)^{3-}$. The anion was isolated as colourless crystalline $Na_3GeS_3(OH) \cdot 8H_2O$. The salt is monoclinic, space group C2/c, with unit cell dimensions a = 31.794(10), b = 6.678(3), c = 14.721(5) Å, β = 110.72(3)°, V = 2923.6 Å^3, Z = 8*. The crystal structure was determined from single-crystal X-ray data (R = 0.058) and shows slightly distorted tetrahedral $GeS_3(OH)^{3-}$ anions linked through an extensive hydrogen bond system to octahedral edge-sharing $Na(OH_2)_6$ and $Na(OH_2)_4S_2$ groups of the cation system. The anion has approximate C_s symmetry, the symmetry of the GeS_3O part is close to C_{3v},. Fig. 2 shows the bond data of the $GeS_3(OH)^{3-}$ ion in the crystal.

$GeS_2(OH)_2^{2-}$ and $GeS_3(OH)^{3-}$ are the first examples of protonated thio-oxoanions. The hydrogen

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*This unit cell is actually a subcell of a larger one with $b' = 2b$, $V' = 2V$. Only the cation–water system is affected by cell doubling [10].

atom positions were uniquely determined from the crystal structure analyses. The remarkably strong basicity of the oxygens distinguishes the ions clearly from the analogous thiophosphates $PS_xO_{4-x}^{3-}$ and thioarsenates $AsS_xO_{4-x}^{3-}$, in which mesomeric stabilization of the PO_{4-x} and AsO_{4-x} fragments favours deprotonation.

The Ge–O bond lengths in the two thio-oxoanions show a considerable increase from about 1.71–1.78 Å observed in normal germanates through 1.812 Å for $GeS_2(OH)_2^{2-}$ to 1.877 Å for $GeS_3(OH)^{3-}$. The Ge–S distances are within the range of the terminal bond lengths (2.11–2.17 Å) in the normal thiogermanates cited above [2–7] with, again, a significant weakening of the bonds within the more negatively charged $GeS_3(OH)^{3-}$.

In the Raman spectra of the solids the Ge–S stretching vibrations are observed at 415 (ν_s; $\nu_1(A_1)$ for C_{2v}) and 454 cm^{-1} (ν_{as}; $\nu_6(B_1)$) for $GeS_2(OH)_2^{2-}$ and at 385 and 417 cm^{-1} for $GeS_3(OH)^{3-}$.

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