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Synthesis of four different antimony(III) *O*,*O*′-dialkyldithiophosphates: Characterization by ^{31}P CP/MAS NMR, single-crystal X-ray diffraction, and adsorption at a stibnite surface (Sb_2S_3)

Anna-Carin Larsson [a,*], Maxim A. Ivanov [b], Andrey V. Gerasimenko [c], Alexander V. Ivanov [b]

[a] Division of Sustainable Process Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden
[b] Institute of Geology and Nature Management, Far Eastern Branch of the Russian Academy of Sciences, 675000 Blagoveschensk, Amur Region, Russia
[c] Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, 690022 Vladivostok, Russia

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ABSTRACT

Four different dialkyldithiophosphate (DTP) ions, $(RO)_2PSS^-$ (R = C_3H_7, *iso*-C_3H_7, *iso*-C_4H_9, and *cyclo*-C_6H_{11}), have been adsorbed on the surface of synthetically prepared stibnite, Sb_2S_3, and studied by means of ^{31}P CP/MAS NMR. Corresponding individual [$Sb\{S_2P(OR)_2\}_3$] complexes have also been synthesized and used for comparison with the surface-adsorbed DTP species. The results show that a low concentration of collector at the surface leads to a chemisorbed monolayer of DTP on the mineral surface. At high concentration of DTP, a surface precipitate of $Sb(DTP)_3$ is formed. ^{31}P CP/MAS NMR and chemical shift anisotropy data indicate that the S—P—S bite angle of the chemisorbed DTP groups on the surface is larger than in the corresponding precipitated complexes and the coordination of the ligands differs. Using single-crystal X-ray diffraction technique, the molecular structure of a solvated form of crystalline *O*,*O*′-di-*cyclo*-hexyldithiophosphate antimony(III) complex has been resolved. In this novel molecular structure, the central antimony atom *S*,*S*′-anisobidentately coordinates three structurally non-equivalent DTP groups, and therefore, the geometry of the [SbS_6] chromophore can be approximated by a distorted octahedron. Besides that, useful correlations between ^{31}P CSA parameters and structural data on this complex were also established.

1. Introduction

Antimony and its compounds have many important applications, e.g., in alloys, in batteries, as flame-retardants, semiconductors, and pigments [1–9]. Antimony trisulfide (Sb_2S_3) has found use, e.g., in various optical and photosensitive applications, for radiolabeling, and as a lubricant [1–9]. The principal source of antimony is the natural mineral stibnite, Sb_2S_3. In the froth flotation of sulfide minerals, ionic *O*,*O*′-dialkyldithiophosphates (DTP) are frequently used reagent collectors. One of the important questions in flotation theory is connected with the fixation modes of ionic dithioreagent collectors (such as dialkyldithiophosphates, alkyldithiocarbonates (*i.e.*, xanthates), and dialkyldithiocarbamates) on the surfaces of sulfide minerals. Previously, using both liquid and solid-state ^{31}P NMR techniques, we have established principally different fixation modes of DTP ions on the surface of both synthetic sphalerite (ZnS) [10] and galena (PbS) [11]. The bridging coordination of DTP groups to two neighboring zinc atoms was suggested in the case of surface zinc(II) complexes on a ZnS surface [10], while there is mainly terminal *S*,*S*′-chelating coordination of DTP ions to one lead atom on a PbS surface [11]. To get an efficient flotation of Sb_2S_3, it is meaningful to understand the interaction between mineral surface and ionic dialkyldithiophosphate collectors.

In this study, we have characterized four different potassium *O*,*O*′-dialkyldithiophosphates adsorbed on the surface of synthetically prepared Sb_2S_3. It is known that Sb(III) is starting to oxidize to Sb(V) at pH above 4 [9]. In order to avoid oxidation, the adsorption experiments were performed at pH 3. ^{31}P CP/MAS NMR was used to study the coordination of DTP groups to the mineral surface. For comparison, $Sb(DTP)_3$ complexes with the same ligands were synthesized and ^{31}P and ^{13}C CP/MAS NMR measurements were taken. Both ^{31}P chemical shifts and chemical shift anisotropy (CSA) were used to characterize the surface coordination.

Additionally, the crystal and molecular structure of tris(*O*,*O*′-di-*cyclo*-hexyldithiophosphato-*S*,*S*′)antimony(III), which is solvated with ethanol, has been determined using the single-crystal X-ray diffraction technique.

* Corresponding author. Address: Division of Sustainable Process Engineering, Department of Civil, Environmental and Natural Resources Engineering, Luleå University of Technology, SE-971 87 Luleå, Sweden. Fax: +46 (0) 920491199.
E-mail address: anna-carin.v.larsson@ltu.se (A.-C. Larsson).

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2. Experimental

2.1. Synthesis of Sb_2S_3

Antimony trisulfide, Sb_2S_3, was synthesized in basically the same way as is previously reported [2]. An excess of thioacetamide was added to a 0.1 M solution of $SbCl_3$ in absolute ethanol. The solution was stirred until the color changed from yellow to red. The mixture was left for 24 h before the precipitate was filtered and washed with ethanol. The red Sb_2S_3 was dried in vacuum at 100 °C until it transformed into the stable black form. The identity of the sample was confirmed by XRD.

2.2. Preparation of surface complexes

Surface adsorption experiments were performed by preparing 0.1 mM aqueous solutions of potassium dialkyldithiophosphates, $K\{S_2P(OR)_2\}$, with R = *n*-propyl, *iso*-propyl, *iso*-butyl, and *cyclo*-hexyl. Antimony trisulfide, Sb_2S_3 (0.8 g), was added to 70 ml of the solutions, and the mixtures were stirred for 1.5 h at pH 3.1. The pH value was controlled by adding a few drops of a 0.1 M NaOH solution as needed. The mixtures were filtered off and dried overnight in a desiccator. For di-*iso*-butyldithiophosphate, an additional adsorption was made with a 3 mM aqueous solution.

2.3. Preparation of polycrystalline complexes

Corresponding $[Sb\{S_2P(OR)_2\}_3]$ complexes (compound **I** – R = *iso*-C_3H_7, **II** – *iso*-C_4H_9, **III** – *cyclo*-C_6H_{11}, and **IV** – C_3H_7) were prepared by mixing ethanol solutions of $SbCl_3$ and $K\{S_2P(OR)_2\}$, analogous to previously described procedures [12]. Light yellow precipitates of compounds **I** and **II** were additionally recrystallized from acetone. The melting points of $Sb(iPrDTP)_3$ (80 °C) and $Sb(iBuDTP)_3$ (123 °C) were in accordance with previously reported values [12–14]. The melting point of a solvated form of $Sb(cHexDTP)_3$ could not be determined. At approximately 180 °C, the solid decomposed into the orange-red polymorph of Sb_2S_3. $Sb(nPrDTP)_3$ was a yellow liquid, and hence, CP/MAS NMR experiments could not be performed.

For X-ray diffraction studies, suitable single crystals of tris(*O*,*O*′-di-*cyclo*-hexyldithiophosphato-*S*,*S*′)antimony(III), which is solvated with ethanol, $[Sb\{S_2P(O\text{-}cyclo\text{-}C_6H_{11})_2\}_3]\cdot 1/3\ C_2H_5OH$ (**III**), were prepared using recrystallization of precipitated complex from warm acetone–ethanol (10:1) solution at 56 °C. Compound **III** was isolated as transparent yellowish crystals of a prismatic shape.

2.4. CP/MAS NMR

Solid-state ^{31}P and ^{13}C CP/MAS NMR experiments [15] were performed on a Varian/Chemagnetics InfinityPlus CMX-360 spectrometer. For the ^{31}P experiments, the operating frequency was 145.719 MHz. The spectrum width was 75 kHz. The spectra were referenced relative to 85% H_3PO_4 (δ = 0 ppm) [16]. The proton $\pi/2$ pulse was 5.0 μs, and contact time was 4 ms (1 ms for R = *cyclo*-hexyl). Number of transients were 16 for the $Sb(DTP)_3$ complexes (512 for R = *cyclo*-hexyl) and 15,000–30,000 for the surface-adsorbed complexes. The spectra of the $Sb(DTP)_3$ complexes were acquired at two different spinning frequencies: 2000 and 3000 Hz, in order to identify the isotropic chemical shifts. The surface-adsorbed complexes were measured only at 4500 Hz.

For the ^{13}C CP/MAS NMR experiments, the operating frequency was 90.5152 MHz. The spectrum width was 100 kHz. The spectra were referenced relative to adamantane (δ = 38.48 ppm [17]). The proton $\pi/2$ pulse and contact time were 4.4 μs and 3 ms, respectively. Number of transients was 16 and spinning frequency 3 kHz.

2.5. Chemical shift anisotropy analysis

Analysis of the ^{31}P chemical shift anisotropy (CSA) was performed in a Mathematica-based program developed by Levitt and co-workers [18]. The input in the program is the intensities of the spinning sidebands, the spinning frequency, the noise level, and the Larmor frequency. The program plots the χ^2-statistics as a function of the two CSA parameters δ_{aniso} and η and gives their values with 68.3% confidence limits.

From the values of δ_{aniso} and η, the principal values of the chemical shift tensor were calculated from the following equations [18]:

$$\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3 \quad (1)$$

$$\delta_{aniso} = \delta_{zz} - \delta_{iso} \quad (2)$$

$$\eta = (\delta_{yy} - \delta_{xx})/\delta_{aniso} \quad (3)$$

where δ_{xx}, δ_{yy}, and δ_{zz} are defined as $|\delta_{zz} - \delta_{iso}| \geqslant |\delta_{xx} - \delta_{iso}| \geqslant |\delta_{yy} - \delta_{iso}|$. δ_{xx}, δ_{yy}, and δ_{zz} were then relabeled as δ_{11}, δ_{22}, and δ_{33} with δ_{11} being the most deshielded value and δ_{33} the most shielded [19]. η = 0 refers to an axially symmetric tensor, with either prolate ($\delta_{aniso} > 0$) or oblate shape ($\delta_{aniso} < 0$), while η = 1 refers to a rhombic tensor. When η is close to 1, the sign of δ_{aniso} can be difficult to determine with certainty. Fig. 1 shows the shape of static NMR spectra for the three different extremes of tensor shape.

The span was also used to define the tensor [19]:

$$\Omega = \delta_{11} - \delta_{33} \quad (4)$$

The confidence limits of δ_{11}, δ_{22}, δ_{33}, and Ω were determined by the partial derivative method [20].

2.6. Crystal structure determination

A suitable single crystal of compound **III**, $[Sb\{S_2P(O\text{-}cyclo\text{-}C_6H_{11})_2\}_3]\cdot 1/3\ C_2H_5OH$, was selected and mounted on glass fibers with epoxy glue. Experimental intensity data were collected at T = 170(1) K on a BRUKER Kappa APEX II diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) [21] (crystal–detector distance 60 mm). A multi-scan absorption correction was applied using SADABS [22]. The unit cell dimensions, additional crystallographic data, and refinement results for the complex are given in Table 1.

The structure was solved by direct methods and refined by least-squares calculation in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were added at ideal positions and refined using a riding model. In solvating ethanol molecules, which are disordered relative to threefold axis, all atoms have the same (0.33333) site occupation factors. Data collection and editing, as well as refinement of unit cell parameters, was per-

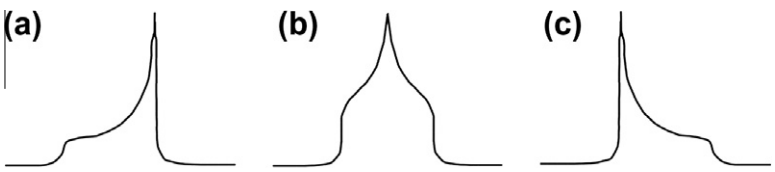

Fig. 1. Shape of static NMR spectra for the cases of prolate (a), rhombic (b), and oblate (c) chemical shift tensors.