



Review

Synthesis, structure determination and calorimetric study of new caesium hydrogen selenate arsenate $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$

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ARTICLE INFO

Article history:

Received 7 July 2008

Received in revised form 7 October 2008

Accepted 14 October 2008

Available online 5 December 2008

Keywords:

Inorganic material

Mixed selenates and arsenates

Crystal structure

IR spectroscopy and calorimetric analyse

ABSTRACT

A new compound, $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$, was synthesized from aqueous solution of $\text{CsHSeO}_4/\text{Cs}_3\text{H}(\text{SeO}_4)_2/\text{H}_3\text{AsO}_4$ (80.5%). The compound was characterized by X-ray single-crystal analysis, with the following crystal data: monoclinic, space group $P2_1$, $a = 5.973(1)\text{Å}$, $b = 13.691(3)\text{Å}$, $c = 11.910(3)\text{Å}$ and $\beta = 94.867(1)^\circ$.

The compound has a unit cell volume $970.39(4)\text{Å}^3$ and two formula units per cell, giving a calculated density of 3.780g cm^{-3} . The structure was solved from 5493 independent reflections and refined with 218 parameters yielded weighted residuals of 0.1243 and 0.0474 based on F^2 and values, respectively.

This compound have a coordination number of caesium of 11, with Cs–O distances from 2.945(7) to 3.915(16) Å. As and Se atoms form the individual tetrahedra with different H-bonding connectivity in this structure. AsO_4 – SeO_4 layers with attached SeO_4 groups are present.

The infrared spectra of the new compound $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$ recorded at room temperature in the frequency range 4000 – 400cm^{-1} confirm the presence of AsO_4^{3-} and SeO_4^{2-} groups in the same crystal. The differential scanning calorimetry (DSC) and the thermogravimetry (TG) curves show two phase transitions at 411 and 418 K in this material.

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1. Introduction

Systematic investigation in the system CsHSeO_4 [1]/ $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ [2–4]/ H_3AsO_4 (80.5%) led to a new mixed oxosalts with the composition $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$. Following the first investigation concerning the synthesis and the crystal structure of

$\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{PO}_4)$ [5] and $\text{K}_4(\text{SO}_4)(\text{HSO}_4)_2(\text{H}_3\text{AsO}_4)$ [6], the $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$ compound is considered to be the tried alkali to enrich this type of compounds.

In the last few years, new mixed hydrogen sulphate-phosphate [7–11], hydrogen sulphate-arsenate [12], hydrogen selenate-phosphate [13,14] and hydrogen selenate-arsenate have been synthesized and structurally characterized. The physical properties above mentioned are strongly connected with the phase transitions of the acidic oxosalts, which are of special interest.

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Table 1
Results of chemical analysis for $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$.

Weight percentage	Cs (%)	Se (%)	As (%)
Calculated	48.13	21.44	6.78
Experimental	46.4 ± 0.5	21.1 ± 0.5	6.5 ± 0.4
Molar ratio	Cs/Se	Cs/As	Se/As
Calculated	1.33	4.00	3.00
Experimental	1.31	4.02	3.07

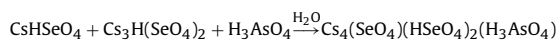
Recently, studies of new hydrogen-bonded systems have been of continuing interest due to the structural and physical properties of these compounds which are, today, oriented and supported by two main observations. The first is related to the dynamics of protons in solids which show ferroelectric or antiferroelectric order and proton spin glasses in the low-temperature phases [15–17]. The second is devoted to the fast-ion transport which is usually observed in the high-temperature phases, leading to a high protonic conductivity in a superprotonic state. An examination in the literature has shown so far no structural study of the title compound.

In this paper, we describe the synthesis and the crystal structure of new mixed caesium selenate hydrogen-selenate arsenate, $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$ (denoted CsSeHSeAs). This compound is isotypic with the corresponding mixed caesium selenate hydrogen-selenate phosphate, $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{PO}_4)$. We have performed X-ray diffraction measurements providing us information about the complete crystal structure at room temperature of this new compound. This structure study is accompanied by infrared measurements in order to confirm the presence of the two anions (SeO_4^{2-} and AsO_4^{3-}) and elucidate the hydrogen bonds in their crystal lattice. The thermal study by differential scanning calorimetry (DSC) and thermogravimetry (TG) was achieved in order to evidence the phase transitions in this compound.

2. Experimental

2.1. Synthesis and characterization

Before the synthesis of $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$, it is necessary to synthesize CsHSeO_4 [1] and $\text{Cs}_3\text{H}(\text{SeO}_4)_2$ [2–4] by reaction of Cs_2CO_3 (99.9%, Merck) and selenic acid (94%), respectively, with a molar ratio 1:2 and 3:4. Crystals gotten from these preparations are used to synthesize the crystal of $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$ from aqueous solution with 0.56 g of caesium hydrogen selenate, 1.38 g of tricesium hydrogen biselenate and an excess of orthoarsenic acid (0.5 g of H_3AsO_4) with a purity of 80.5% according to the reaction:



To obtain compound with a ratio Se:As = 3:1 and to suppress the dissociation of HSeO_4^- , an excess of H_3AsO_4 was used. Slow evaporation of water at 298 K yielded colourless, transparent and stretched parallelepipedic crystals after a few days later with a size of about 0.05 mm × 0.075 mm × 0.225 mm. Several recrystallizations were necessary to obtain single crystals suitable for X-ray study. The ratio of Cs/Se and Cs/As of this compound is determined by chemical analysis using the method of ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) and compared with the calculated one (Table 1). The composition of the compound was also confirmed by refinement of the crystal structure. The compound is stable in the dry air. From solution with higher percentage of selenium (>80%), caesium hydrogen selenate (CsHSeO_4) and tricesium hydrogen diselenate ($\text{Cs}_3\text{H}(\text{SeO}_4)_2$) are recrystallized. A lower $\text{HSeO}_4:\text{H}_2\text{AsO}_4$ ratio of 55:45 led to the precipitation of CsH_2AsO_4 . Due to incongruent crystallization, mixture of two phases with CsHSeO_4 and CsH_2AsO_4 was found in some cases.

Infrared absorption spectra of suspensions of crystalline powders in KBr were recorded at room temperature using an IR-470 Shimadzu Spectrophotometer in the range 400–4000 cm^{-1} . Differential scanning calorimetry (DSC) has been performed on a METTLER TOLEDO DSC 822^o between 293 and 573 K; a polycrystalline sample of 6 mg was placed in a hermetic aluminum cell into a nitrogen atmosphere. Data were collected with a speed of heat 5 K min^{-1} , under flowing nitrogen.

2.2. X-ray diffraction and data collection

Single crystal suitable for X-ray structure analysis was selected under a polarization microscope. X-ray diffraction intensity data were obtained on a Kappa CCD diffractometer (Bruker-Nonius) using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. Crystal data and experimental conditions are reported in Table 2. Data were collected at room temperature (293 K) from an as-synthesized specimen measuring 0.05 mm × 0.075 mm × 0.225 mm in size. The unit cell parameters optimized by least-squares refinement were calculated and refined using indexation of the collected intensities. The raw intensity data were corrected for Lorentz and polarizing effect before refinement of the structure.

The empirical absorption correction was applied using a SCALEPACK method [18]. The lattice parameters of the crystal obtained from single-crystal diffractometer measurement are: $a = 5.973(1) \text{ \AA}$, $b = 13.691(3) \text{ \AA}$, $c = 11.910(3) \text{ \AA}$ and $\beta = 94.867(10)^\circ$. With a non-centrosymmetric space group $P2_1$. Atomic scattering factors and anomalous dispersion parameters were taken from the International Tables for X-Ray Crystallography [19]; 12,649 reflections were collected in the whole Ewald sphere for $2.98^\circ < \theta < 32.02^\circ$ of which 6585 reflections are independent and 5493 had an intensity of $I > 2\sigma(I)$. The heavy-atom method was used to solve the structure. The chemical data and the results of crystal structure determinations are listed in Table 2. The structure was successfully developed in the non-centrosymmetric space group $P2_1$. We solved the structure by first locating the Cs by Patterson methods and subsequently the Se, As and O atom positions were deduced from difference Fourier maps. Patterson methods calculations were performed using the SHELXS-97 program [20] and the Fourier synthesis calculations were deduced using an adapted version of SHELXL-97 program [21]. There are two formula units in the unit cell and all the atoms are in general positions. Hydrogen-bonded oxygen atoms were identified on the basis of bond length considerations, rather than from a refinement of proton positions from X-ray data. Bonding considerations were also utilized to distinguish between Se and As sites. The five acidic hydrogen atoms required in a unit cell by the chemical formula also appeared in general positions. The least-squares refinement, including isotropic hydrogen atoms, converge to an acceptable final agreement factors $R_1 = 4.74\%$ and $wR_2 = 12.43\%$, obtained by fitting 218 parameters. A last difference Fourier series gave only intensity peaks inferior or equal to 1.925 e \AA^{-3} with respective distances from Se(1) and As atoms equal to 0.26 and 0.43 \AA .

The chemical crystal data and the results of crystal structure are summarized in Table 2. The final atomic coordinates are given in Tables 3 and 4.

Table 2
Main crystallographic features, X-ray diffraction data collection parameters and final results for $\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$.

Formula	$\text{Cs}_4(\text{SeO}_4)(\text{HSeO}_4)_2(\text{H}_3\text{AsO}_4)$
Weight	1104.48 g mol^{-1}
Colour	Colourless
Crystal system	Monoclinic
Space group	$P2_1$
Temperature	293(2) K
<i>a</i>	5.973(1) \AA
<i>b</i>	13.691(3) \AA
<i>c</i>	11.910(3) \AA
β	94.867(10)°
<i>V</i>	970.39(4) \AA^3
<i>Z</i>	2
Diffractometer (Bruker-Nonius)	Kappa CCD
Theta range	2.98–32.02°
λ (Mo $\text{K}\alpha$)	0.71073 \AA
Max. crystal dimensions (mm)	0.05 × 0.075 × 0.225
ρ_{cal}	3.780 g cm^{-3}
ρ_{exp}	3.782 g cm^{-3}
<i>F</i> (000)	488
μ (mm^{-1})	7.419
Monochromator	Graphite
$h_{\text{min}}, k_{\text{min}}, l_{\text{min}}$	–8, –20, –17
$h_{\text{max}}, k_{\text{max}}, l_{\text{max}}$	8; 20; 17
Parameters of thermal agitation	$R_{\text{int}} = 0.0450$ and $R_\sigma = 0.0514$
Reflections collected	12,649
Independent reflections	6585
Reflection with $I > 2\sigma(I)$	5493
Parameters	218
R_1^a [$F^2 > 2\sigma(F^2)$]	0.0474
wR_2^a (F^2)	0.1243
<i>S</i>	1.053
$\Delta\rho$ (max) and $\Delta\rho$ (min)	1.925 and –2.138 e \AA^{-3}

$$^a R_1 = (\sum |F_o - |F_c|| / \sum |F_o| \text{ and } wR_2 = (\sum [W(F_o^2 - F_c^2)] / [W(F_o^2)])^{1/2}.$$

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