JOURNAL OF SOLID STATE CHEMISTRY **141**, 317–322 (1998)
ARTICLE NO. SC987921

New Cesium Hydrogen Selenate Phosphates: Synthesis and Crystal Structures

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Received March 16, 1998; in revised form May 28, 1998; accepted June 8, 1998

Three new compounds, $Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$ (I), $Cs_3(HSeO_4)_2(H_2PO_4)$ (II), and $Cs_5(HSeO_4)_3(H_2PO_4)_2$ (III), were synthesized from water solutions of $CsHSeO_4/CsH_2PO_4$. According to X-ray single-crystal analysis, the compounds have the following crystal data: I, monoclinic, space group $P2_1$, $a = 5.915(1)$ Å, $b = 13.797(3)$ Å, $c = 11.828(2)$ Å, $\beta = 95.11(3)^\circ$, $V = 961.4$ Å^3, $Z = 2$, $R_1 = 0.0384$; II, monoclinic, space group $P2_1/n$, $a = 20.281(8)$ Å, $b = 8.039(4)$ Å, $c = 9.160(4)$ Å, $\beta = 99.96(4)^\circ$, $V = 1470.9$ Å^3, $Z = 4$, $R_1 = 0.0580$; III, monoclinic, space group $C2/c$, $a = 33.855(8)$ Å, $b = 7.978(2)$ Å, $c = 9.217(2)$ Å, $\beta = 101.00(2)^\circ$, $V = 2443.7$ Å^3, $Z = 4$, $R_1 = 0.0519$. All three compounds have in common a coordination number of cesium of 10 or 10+1, with Cs–O distances from 2.9 to 3.8 Å. P and Se atoms form the individual tetrahedra with different H-bonding connectivity in structures I–III. PO_4–SeO_4 layers with attached SeO_4 groups are present in I. Structure II contains a three-dimensional hydrogen bonding network, whereas structure III is characterized by PO_4–SeO_4 bands to which additional SeO_4 tetrahedra are attached.

1. INTRODUCTION

The structures of many metal hydrogen sulfates, selenates, and phosphates have been investigated in detail using X-ray and neutron diffraction methods. Some of these compounds are known to undergo phase transitions to superprotonic or ferroelectric phases (1, 2). Recently, crystal structures and superprotonic phase transitions for a number of $CsHSO_4$–CsH_2PO_4 compounds were reported (3–6). Due to the close similarities in chemical compositions and crystal chemistry of sulfates and selenates, one could expect the analogous mixed selenate phosphate compounds to exist and exhibit properties as in the respective metal sulfate phosphates.

In fact, our systematic investigation of the systems MHSeO$_4$–MH$_2$PO$_4$ (M = alkali metal) resulted in the synthesis of new compounds for M = Na, K, Rb, and Cs with selenate to phosphate ratios of 3:1, 2:1, 3:2, and 1:1. In this paper, we describe the synthesis and crystal structures of three new cesium hydrogen selenate phosphates, $Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$ (**I**), $Cs_3(HSeO_4)_2(H_2PO_4)$ (**II**), and $Cs_5(HSeO_4)_3(H_2PO_4)_2$ (**III**). Compound **II** is isotypic with the corresponding cesium hydrogen sulfate phosphate (3), whereas the other two form new structure types.

EXPERIMENTAL

Synthesis

The crystalline phases of cesium hydrogen selenate phosphates were obtained from solutions of Cs_2CO_3 (p.a.) in a mixture of 70% H_2SeO_4 and 65% H_3PO_4. X-ray powder diffraction (Co$K\alpha$ radiation, DRON-4 diffractometer) was used to control the purity of the crystalline phases. To obtain compounds with different ratios Se:P = 3:1, 2:1, and 3:2, the molar ratio of H_2SeO_4:H_3PO_4 was varied. An excess of H_3PO_4 was used to suppress the dissociation of $HSeO_4^-$. The selenate to phosphate ratios in solution should exceed those in the crystals because of the incongruent type of crystallization. For example, $Cs_5(HSeO_4)_3(H_2PO_4)_2$ (S:P = 3:2) was crystallized from solution with a $HSeO_4$:H_2PO_4 ratio of 65:35. The corresponding $HSeO_4$:H_2PO_4 ratios for the synthesis of $Cs_3(HSeO_4)_2(H_2PO_4)$ and $Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$ were 70:30 and 77:23, respectively. From solutions with higher H_2SeO_4 content ($>80\%$), pure cesium hydrogen selenate, $CsHSeO_4$, was obtained. A lower $HSeO_4$:H_2PO_4 ratio of 55:45 led to the precipitation of CsH_2PO_4. Due to incongruent crystallization, mixtures of two phases were found in some cases. The exact composition of the compounds was determined by X-ray single-crystal analysis. The compounds are stable in air and form plates (**I** and **II**) or blocks (**III**).

Crystal Structure Determination

Single-crystal X-ray data were collected at room temperature using two different diffractometers, Stoe STADI-4

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0022-4596/98 $25.00

(**I** and **II**) and Enraf-Nonius CAD-4 (**III**) (Mo$K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å, ω–2θ scan mode). Unit cell parameters were refined using sets of 24 centered reflections. The empirical absorption corrections were applied using ψ scan data for 6–8 reflections.

The structures were solved by direct methods (SHELXS-86 (7)) and subsequent Fourier syntheses. Hydrogen atoms were not determined or calculated. All non-hydrogen atoms were refined anisotropically (SHELXL-93 (8)). The crystal data and details of data collection and refinement for compounds **I**–**III** are summarized in Table 1. Somewhat higher final R values are caused by the presence of heavy atoms and by higher background due to the fluorescence of Se under Mo$K\alpha$ radiation. The atomic coordinates and equivalent isotropic thermal parameters are given in Table 2, and selected bond distances are listed in Table 3.

GENERAL CONSIDERATIONS

In general, the composition of crystals does not correspond to that of the solution. For that reason it is not simple to get single-phase compounds from these systems. The most successful way was to isolate the crystalline phase after the initial stage of crystallization, because further cystallization sometimes produced a mixture of two solid phases. In some cases, the crystallization of pure $CsHSeO_4$ from solution containing selenate and phosphate in 3:1 ratio was observed. Apparently, such phenomena are caused by low values of the formation enthalpy of the mixed phases from the components, cesium hydrogen selenates and cesium hydrogen phosphates.

It is worth to noting that in most cesium structures containing two different anions, selenium/phosphorus and sulfur/phosphorus atoms occupy different positions (3, 6), whereas positions with a mixed occupancy are characteristic for mixed hydrogen sulfate phosphates of all other alkali metals (9) and only in one case for a cesium derivative (5). In contrast to the sulfate/phosphate system, the positions of selenium and phosphorus could not be confused due to large differences in the scattering factors of Se and P.

On the other hand, determination of the hydrogen positions was impossible for **I**–**III** containing both selenium and cesium. Therefore, the hydrogen-bonding systems were derived on the basis of X–O and O···O distances using the relationships reviewed in (10). It is well known that typical Se–OH distances, 1.7 Å, are about 0.1 Å longer than Se–O, 1.6 Å. If a hydrogen disorder is present, the Se–O distances have intermediate values, i.e., 1.67 Å for half-donor and half-acceptor functions (10).

The lengths of the O···O hydrogen bonds are listed in Table 4. Hydrogen bonds of large and middle strength were found in the structures under investigation, the O···O distances being in the range 2.47–2.79 Å, with the only exception the hydrogen bond of half occupancy in structure **III** (O···O distance 3.02 Å). As a rule, the shorter O···O distances correspond to the strongly disordered hydrogen bonds. However, bonds with partly disordered H were inferred in some cases from the intermediate O···O distances.

TABLE 1
Crystallographic Data and Details of Structure Refinements for I–III

	$Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$	$Cs_3(HSeO_4)_2(H_2PO_4)$	$Cs_5(HSeO_4)_3(H_2PO_4)_2$
FW	1060.50	783.63	1290.61
Space group	$P2_1$	$P2_1/n$	$C2/c$
a (Å)	5.915(1)	20.281(8)	33.855(8)
b (Å)	13.797(3)	8.039(4)	7.978(2)
c (Å)	11.828(2)	9.160(4)	9.217(2)
β (deg)	95.11(3)	99.96(4)	101.00(2)
V (Å^3)	961.4(3)	1471(2)	2444(1)
Z	2	4	4
μ (cm^{-1})	133.51	124.99	120.64
ρ_{calcd} (g/cm^3)	3.663	3.539	3.507
Crystal size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.3 × 0.3	0.6 × 0.3 × 0.3
Temperature (K)	293(2)	293(2)	293(2)
Diffractometer	STADI-4	STADI-4	CAD-4
θ_{max} (deg)	27	26	30
Total reflections	2474	2960	3763
Unique reflections	2441	2885	3549
Reflections with $I > 2\sigma(I)$	2376	2129	2222
Number of parameters	219	163	138
wR_2[a]	0.1113	0.1661	0.1363
R_1[a]	0.0384	0.0580	0.0519

[a] R values are defined as $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$ and $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

TABLE 2

Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2)

Atom	x	y	z	U_{eq}
$Cs_4(SeO_4)(HSeO_4)_2(H_2PO_4)$ (**I**)				
Cs(1)	0.2955(2)	0.82850(9)	0.09503(8)	0.0297(3)
Cs(2)	0.2045(2)	0.55025(9)	− 0.09106(8)	0.0303(3)
Cs(3)	0.2688(2)	0.57194(9)	0.36358(10)	0.0295(2)
Cs(4)	0.7695(2)	0.31090(8)	0.36387(8)	0.0319(3)
Se(1)	0.7504(3)	0.8204(1)	0.3697(1)	0.0245(4)
Se(2)	0.7212(2)	0.5731(2)	0.1447(1)	0.0217(3)
Se(3)	0.7781(2)	0.8047(1)	0.8575(1)	0.0226(4)
P	0.7494(8)	0.5589(4)	0.6391(4)	0.025(1)
O(1)	0.869(2)	0.724(1)	0.428(1)	0.041(3)
O(2)	0.837(2)	0.915(1)	0.446(1)	0.047(3)
O(3)	0.822(2)	0.831(1)	0.2402(8)	0.039(3)
O(4)	0.474(2)	0.813(1)	0.3699(8)	0.042(3)
O(5)	0.475(2)	0.6248(8)	0.1390(8)	0.032(2)
O(6)	0.776(2)	0.516(1)	0.2618(9)	0.045(3)
O(7)	0.761(2)	0.512(1)	0.032(1)	0.054(4)
O(8)	0.923(2)	0.6627(9)	0.144(1)	0.036(3)
O(9)	1.020(2)	0.7514(9)	0.8597(9)	0.037(3)
O(10)	0.716(2)	0.867(1)	0.742(1)	0.055(4)
O(11)	0.744(2)	0.858(1)	0.9738(9)	0.044(3)
O(12)	0.579(2)	0.7108(9)	0.8568(9)	0.035(2)
O(13)	0.677(2)	0.5490(8)	0.7568(8)	0.039(3)
O(14)	0.663(2)	0.478(1)	0.5579(9)	0.037(3)
O(15)	1.012(1)	0.566(1)	0.6328(8)	0.037(2)
O(16)	0.655(2)	0.656(1)	0.583(1)	0.043(3)
$Cs_3(HSeO_4)_2(H_2PO_4)$ (**II**)				
Cs(1)	0.32343(7)	0.1341(2)	0.3988(1)	0.0475(4)
Cs(2)	0.32640(6)	− 0.1392(2)	0.8794(1)	0.0423(4)
Cs(3)	0.49889(8)	0.4018(1)	0.2549(1)	0.0372(3)
Se(1)	0.16062(9)	0.1356(2)	0.0671(2)	0.0317(5)
Se(2)	0.15848(9)	− 0.1310(2)	0.5751(2)	0.0322(5)
P	0.4961(3)	− 0.863(5)	0.2494(4)	0.024(2)
O(1)	0.1681(7)	0.244(2)	0.226(1)	0.043(4)
O(2)	0.1017(9)	0.001(2)	0.058(2)	0.068(5)
O(3)	0.1441(9)	0.261(2)	− 0.070(1)	0.067(5)
O(4)	0.2337(8)	0.046(2)	0.071(2)	0.080(6)
O(5)	0.1639(8)	− 0.245(2)	0.724(1)	0.046(4)
O(6)	0.152(1)	− 0.260(2)	0.432(1)	0.079(6)
O(7)	0.0948(9)	− 0.015(2)	0.555(2)	0.073(5)
O(8)	0.2257(9)	− 0.023(2)	0.588(2)	0.082(6)
O(9)	0.4742(6)	0.022(2)	0.369(1)	0.030(3)
O(10)	0.5216(7)	0.025(2)	0.133(1)	0.038(3)
O(11)	0.4386(7)	− 0.194(2)	0.172(1)	0.044(4)
O(12)	0.5535(8)	− 0.197(2)	0.326(1)	0.054(4)
$Cs_5(HSeO_4)_3(H_2PO_4)_2$ (**III**)				
Cs(1)	0.09868(2)	0.5926(1)	0.04972(9)	0.0350(3)
Cs(2)	0	1.1507(2)	0.2500	0.0342(3)
Cs(3)	0.20608(2)	0.8620(1)	0.3243(1)	0.0436(3)
Se(1)	0	0.6490(2)	0.2500	0.0276(4)
Se(2)	0.30478(3)	0.8659(2)	0.1413(1)	0.0293(3)
P	0.10254(8)	1.0819(3)	0.0437(3)	0.0254(6)
O(1)	− 0.0006(3)	0.768(1)	0.1067(9)	0.047(2)
O(2)	0.0397(3)	0.531(1)	0.273(1)	0.062(3)
O(3)	0.2991(2)	0.755(1)	0.2864(9)	0.043(2)
O(4)	0.3425(3)	0.990(1)	0.179(1)	0.071(3)
O(5)	0.2634(3)	0.970(2)	0.090(1)	0.082(4)
O(6)	0.3113(4)	0.736(2)	0.014(1)	0.079(4)
O(7)	0.0872(2)	0.973(1)	− 0.0932(8)	0.030(2)
O(8)	0.1150(2)	0.971(1)	0.1810(8)	0.035(2)
O(9)	0.1382(3)	1.186(1)	0.0174(8)	0.041(2)
O(10)	0.0690(3)	1.202(1)	0.0719(9)	0.037(2)

TABLE 3

Bond Distances (Å) in the Selenium and Phosphorus Tetrahedra

$Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$		$Cs_3(HSeO_4)_2(H_2PO_4)$		$Cs_5(HSeO_4)_3(H_2PO_4)_2$	
X–O	*d*	*X*–O	*d*	*X*–O	*d*
Se(1)–O(1)	1.63(1)	Se(1)–O(1)	1.68(1)	Se(1)–O(1)	1.625(8)
Se(1)–O(2)	1.64(1)	Se(1)–O(2)	1.60(1)	Se(1)–O(2)	1.621(9)
Se(1)–O(3)	1.632(9)	Se(1)–O(3)	1.60(1)		
Se(1)–O(4)	1.64(1)	Se(1)–O(4)	1.64(1)		
Se(2)–O(5)	1.62(1)	Se(2)–O(5)	1.63(1)	Se(2)–O(3)	1.643(9)
Se(2)–O(6)	1.60(1)	Se(2)–O(6)	1.66(1)	Se(2)–O(4)	1.60(1)
Se(2)–O(7)	1.61(1)	Se(2)–O(7)	1.58(1)	Se(2)–O(5)	1.621(9)
Se(2)–O(8)	1.72(1)	Se(2)–O(8)	1.60(1)	Se(2)–O(6)	1.616(9)
Se(3)–O(9)	1.607(9)				
Se(3)–O(10)	1.63(1)				
Se(3)–O(11)	1.59(1)				
Se(3)–O(12)	1.75(1)				
P–O(13)	1.50(1)	P–O(9)	1.53(1)	P–O(7)	1.538(8)
P–O(14)	1.53(1)	P–O(10)	1.55(1)	P–O(8)	1.537(8)
P–O(15)	1.56(1)	P–O(11)	1.52(1)	P–O(9)	1.522(8)
P–O(16)	1.57(1)	P–O(12)	1.53(2)	P–O(10)	1.546(8)

DESCRIPTION OF THE STRUCTURES

The selenate to phosphate ratio in the three new compounds ranges from 3:1 to 3:2. Due to the ionic character of the Cs–O bonding, we prefer not to describe the CsO_n polyhedra in detail. Therefore, only the cesium coordination numbers and the ranges of Cs–O distance are given.

$Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$ (**I**)

In this structure there are four crystallographically independent cesium atoms, three Se tetrahedra, and one phosphorus tetrahedron (Fig. 1). All Cs atoms have 10 shorter and one longer Cs–O contacts: Cs(1), 2.95–3.51, 3.77 Å; Cs(2), 2.99–3.52, 3.71 Å; Cs(3), 3.11–3.53, 3.65 Å; Cs(4), 3.08–3.58, 3.62 Å. The Se(1) atom is surrounded by four oxygen atoms at Se–O distances in a very narrow range of 1.63–1.64 Å. All oxygen atoms in the Se(1)O_4 tetrahedron are involved in hydrogen bonds as acceptors. The Se–O

TABLE 4

Hydrogen Bonds [Å] in I–III

$Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$		$Cs_3(HSeO_4)_2(H_2PO_4)$		$Cs_5(HSeO_4)_3(H_2PO_4)_2$	
O···O	*d*	O···O	*d*	O···O	*d*
O(8)···O(3)	2.67(2)	O(1)···O(11)	2.55(2)	O(1)···O(10)	2.58(1)
O(12)···O(13)	2.62(2)	O(6)···O(4)	2.79(3)	O(3)···O(9)	2.57(1)
O(14)···O(4)	2.59(2)	O(9)···O(9′)	2.47(2)	O(7)···O(8)	2.48(1)
O(15)···O(2)	2.48(2)	O(10)···O(10′)	2.47(2)	O(5)···O(6)	3.02(2)
O(16)···O(1)	2.51(1)	O(12)···O(5)	2.61(2)		

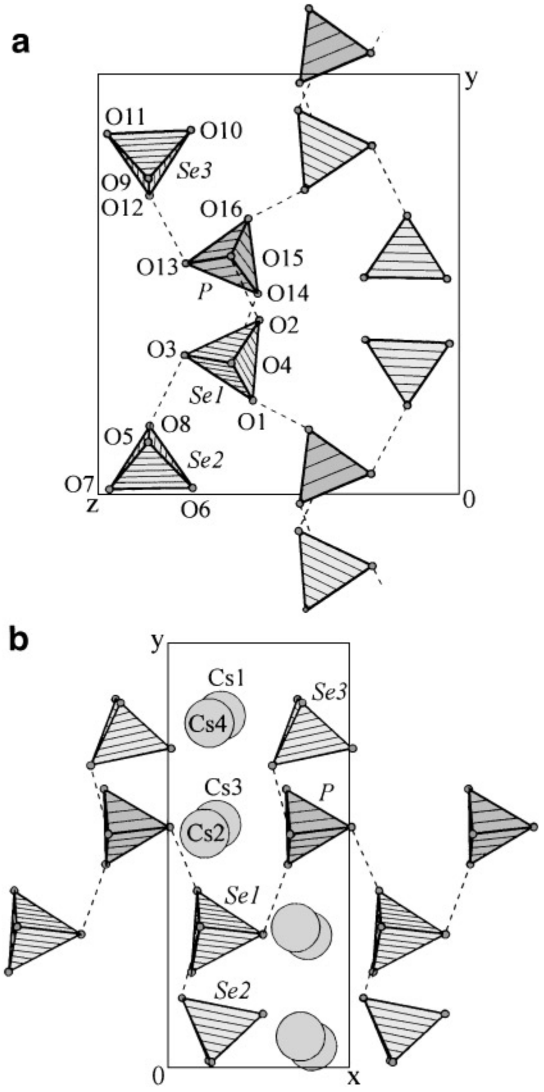

FIG. 1. Structure of $Cs_4(SeO_4)(HSeO_4)_2(H_2PO_4)$. Hydrogen-bonding system consisting of corrugated layers (Se(1) and P) with tetrahedral branches (Se(2), Se(3)): (a) projection in the x direction; (b) zigzag chain extended in the x direction.

distances in the Se(2) and Se(3) tetrahedra are strongly differentiated, with one distance in each longer than 1.7 Å, which can be attributed to the typical Se–OH bond. The Se(2) tetrahedron is hydrogen-bonded to the Se(1) tetrahedron by the hydrogen bond O(8)···O(3), and the Se(3) tetrahedron is attached to the P tetrahedron by O(12)···O(13). The phosphorus tetrahedron has one shorter P–O distance (P–O(13), 1.50 Å) and three elongated P–O distances (1.53–1.57 Å). Taking into account the short distances for the Se(1) tetrahedron, one can assume that all three elongated P–O distances correspond to the hydrogen donor functions of O atoms. Therefore, the composition of compound **I** should be described as $Cs_4(SeO_4)(HSeO_4)_2(H_3PO_4)$ rather than $Cs_4(HSeO_4)_3(H_2PO_4)$ as assumed in the earlier stage of investigation. Apparently, this is the first documented case of a coexistence of SeO_4^{2-} and H_3PO_4 in the same structure. Such an interpretation should be supported by direct determination of the position of the hydrogen atoms, which is not the case for structure **I**. However, according to the preliminary X-ray study of the NH_4HSeO_4–$NH_4H_2PO_4$ system, the 1:1 compound contains both SeO_4^{2-} and H_3PO_4 species, $(NH_4)_2(SeO_4)(H_3PO_4)$.

The whole hydrogen-bonding system can be described as corrugated layers composed of Se(1) and P tetrahedra to which the terminal tetrahedra Se(2) and Se(3) are attached. The layers are built up from Se(1)–P zigzag chains (O(15)···O(2) and O(14)···O(4)) going in the x direction and being connected to each other by O(16)···O(1) hydrogen bonds. The hydrogen bonds O(8)···O(3) (2.67 Å) and O(12)···O(13) (2.62 Å) which link the Se(2) and Se(3) tetrahedra to the P–Se(1) layer are longer than those within the layers, 2.48–2.59 Å.

$Cs_3(HSeO_4)_2(H_2PO_4)$ (**II**)

This structure (Fig. 2) is isotypic with the analogous cesium sulfate phosphate, $Cs_3(HSO_4)_2(H_2PO_4)$ (3). The

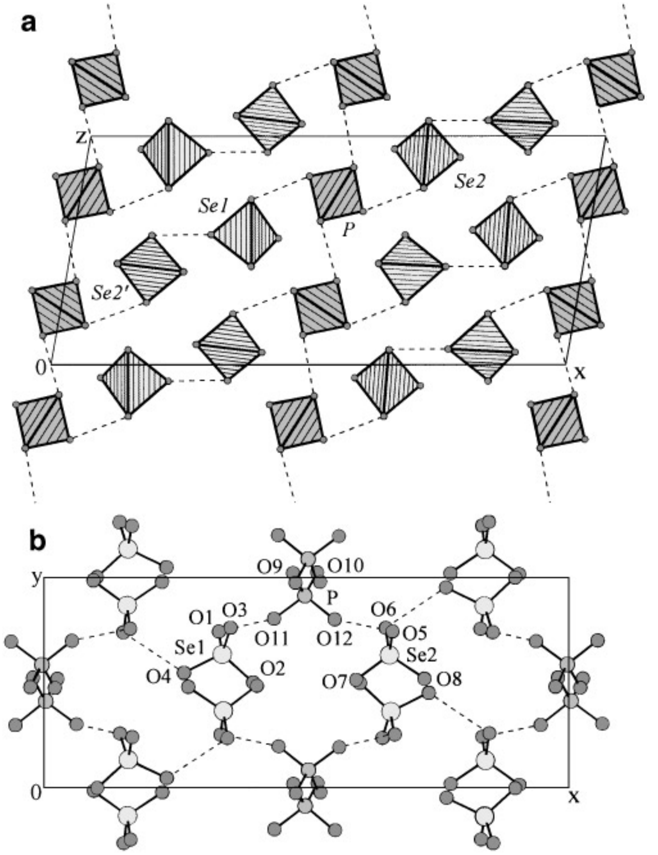

FIG. 2. Structure of $Cs_3(HSeO_4)_2(H_2PO_4)$. (Cs atoms are not shown): (a) polyhedral presentation of the structure in the y direction; (b) $xy0$ projection with atom labeling, showing the tetrahedral connectivity P–Se(1)–Se(2)–P.

three crystallographically independent Cs atoms are coordinated by 11 oxygen atoms. Two of them, Cs(1) and Cs(3), are surrounded by oxygen atoms at distances between 3.00 and 3.55 Å. Cs(2) has 10 shorter and one longer Cs–O contacts, 3.10–3.49 and 3.72 Å. Se(1) is coordinated by four oxygen atoms, with Se–O distances between 1.60 and 1.68 Å, O(1) and O(4) being involved in the hydrogen bonds O(1)···O(11) and O(6)···O(4), which is in line with the longer Se–O distances, 1.68 and 1.64 Å, respectively. The Se–O distances in the Se(2) tetrahedron range from 1.58 to 1.66 Å. Two oxygen atoms at longer distances, Se(2)–O(5), 1.63 Å, and Se(2)–O(6), 1.66 Å, participate in the hydrogen bonds, O(12)···O(5), 2.61 Å, and O(6)···O(4), 2.79 Å. For both selenium tetrahedra, the elongated Se–O distances are shorter than typical Se–OH distances, apparently due to hydrogen disorder. In the phosphorus tetrahedron four P–O bonds have a narrow range of lengths between 1.52 and 1.55 Å, probably due to hydrogen disorder. In fact, the hydrogen bonds O(9)···O(9′) and O(10)···O(10′) are symmetrically disordered with both O···O distances 2.47 Å.

The hydrogen-bonding system can be interpreted as consisting of P tetrahedra chains (connected by the shorter O(9)···O(9) and O(10)···O(10) hydrogen bonds) which are linked by hydrogen bonds via two Se tetrahedra (in the sequence –P–Se(1)–Se(2)–P–) to the neighboring P chains situated by turns at heights $\pm 0.5b$ (Fig. 2b). In this way, a three-dimensional hydrogen-bonding connectivity is present in this structure.

$Cs_5(HSeO_4)_3(H_2PO_4)_2$ **(III)**

There are three crystallographically independent Cs atoms (Cs(2) on the twofold axis), two Se tetrahedra (Se(1) on the twofold axis) and one P tetrahedron (Fig. 3). Cesium atoms have the following CNs and Cs–O distances: Cs(1), 9 + 1, 3.00–3.54, 3.77 Å; Cs(2), 10, 3.13–3.36 Å; Cs(3), 10 + 1, 3.12–3.44, 3.75 Å. Two Se(1)–O(1) bonds are slightly elongated to 1.63 Å, because O(1) is involved in the hydrogen bond O(1)···O(10). Se(2) has only one longer distance, Se(2)–O(3), 1.64 Å, with O(3) participating in the O(3)···O(9) hydrogen bond. All oxygen atoms of the P tetrahedron take part in hydrogen bonds. O(7) and O(8) connect phosphorus tetrahedra with each other via an O(7)···O(8) hydrogen bond. Two other oxygens, O(9) and O(10), participate in the above-mentioned hydrogen bonds between Se and P tetrahedra. One additional hydrogen bond should be present in the structure due to the stoichiometry of the compound. According to O···O distance analysis, it could be O(5)···O(6) with half-hydrogen occupancy and, consequently, a long distance of 3.02 Å, as compared with other O···O distances, 2.48–2.58 Å.

The hydrogen-bonding system consists of two parallel chains of P tetrahedra extended in the *z* direction and linked by Se(1) tetrahedra. Se(2) tetrahedra are attached to each phosphorus tetrahedron forming the branches (Fig. 3b). The basic hydrogen-bonding system can be described as a band of P–Se(1) tetrahedra with branches, Se(2). The bands are

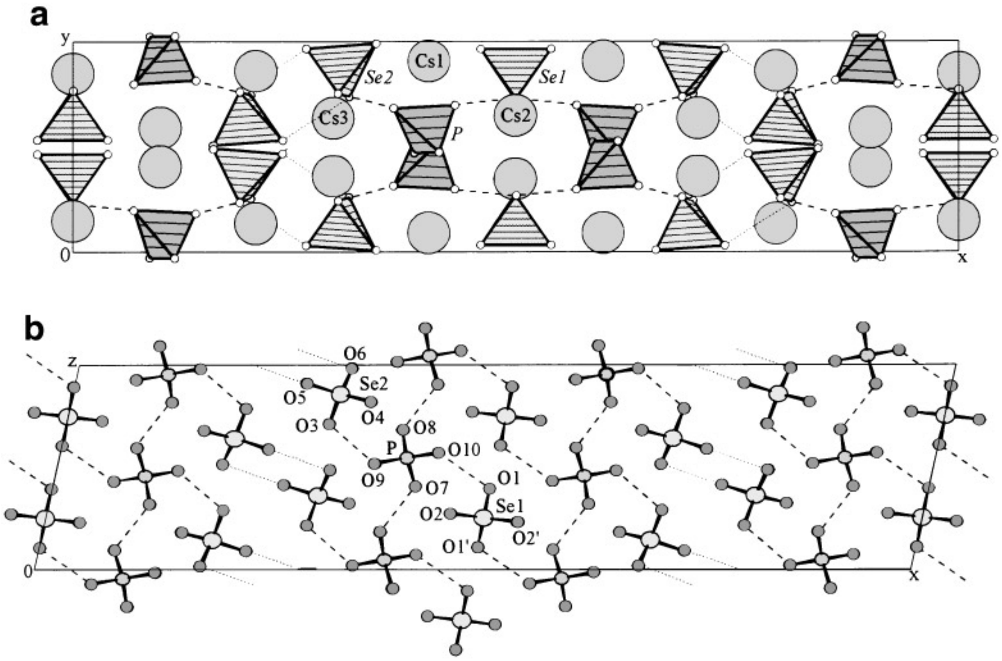

FIG. 3. Structure of $Cs_5(HSeO_4)_3(H_2PO_4)_2$: (a) projection in the *z* direction; (b) *x*0*z* projection and atom labeling (Cs atoms are not shown).

weakly connected to each other by hydrogen bonds of half-occupancy (Fig. 3).

DISCUSSION OF THE STRUCTURES

The new cesium selenate phosphates have many features in common. The coordination of Cs is very similar in all structures, CNs being 10 or 11 (10 + 1) and Cs–O distances ranging from 2.9 to 3.8 Å. In contrast to the ordered structures of $CsHSeO_4$ (11) and CsH_2PO_4 (12), the disordered hydrogen bonds were found around P tetrahedra in most cases and around Se tetrahedra in a few cases. Phosphorus tetrahedra are always four hydrogen connected, forming P–P or P–Se tetrahedra chains to which additional Se tetrahedra are attached. Generally, the Se and P tetrahedra attain the individual connectivity patterns, two and four H bonds, which are present in $CsHSeO_4$ and CsH_2PO_4, respectively.

It is interesting to note that only compound **II** is isotypic with the corresponding cesium hydrogen sulfate phosphate (3). The description of separate structure elements such as hydrogen-bonded P–Se–Se–P or P–P tetrahedra chains for $Cs_3(HXO_4)_2(H_2PO_4)$ are nearly the same for $X = \mathrm{Se}$ as for $X = \mathrm{S}$, with only small differences caused by replacement of S by Se.

Compound **III** has a similar composition (Se:P = 3:2), as recently described for $Cs_5(HSO_4)_3(H_2PO_4)_2$ (6). Even the linear dimensions of the unit cells are very close in both structures. However, the difference in the values of monoclinic angles makes these two structures not isotypic in spite of the same space group. This was additionally proved by comparison of the hydrogen-bonding systems. Compound **I** differs structurally from the other known sulfate phosphate derivatives. It contains two types of Se tetrahedra, SeO_4^{2-} and $HSeO_4^-$, and a H_3PO_4 molecule. Therefore, it has to be referred to as a H_3PO_4 adduct of the mixed cesium selenate hydrogen selenate. The best known examples of such selenates with H:SeO_4 ratio less than one are $M_3H(SeO_4)_2$ ($M = \mathrm{K}$, NH_4, Rb, and Cs (10)). An additional example for an ammonium derivative is $(NH_4)_4H_2(SeO_4)_3$ (13). All these compounds show phase transitions to a superprotonic state at elevated temperatures.

The phase transitions to superprotonic phases have also been found for all cesium hydrogen sulfate phosphates (4,5). One can expect to find similar transitions in selenate/phosphate systems. In fact, our preliminary experiments show a phase transition in compound **I** at 130 ± 3°C. Investigations of phase transitions in **I** and other metal hydrogen selenate phosphates as well as neutron diffraction measurements are in progress.

ACKNOWLEDGMENTS

Financial support from the Deutsche Forschungsgemeinschaft (DFG), Fonds der Chemischen Industrie (FCI), and Russian Foundation for Basic Research (No. 96-03-00084) is gratefully acknowledged.

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