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Crystal Structures, Infrared-Spectra, and Thermal Behavior of Calcium Hydrogenselenite Monohydrate, $Ca(HSeO_3)_2 \cdot H_2O$, and Dicalcium Diselenite Bis(hydrogenselenite), $Ca_2(HSeO_3)_2(Se_2O_5)$

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Calcium hydrogenselenite monohydrate and dicalcium diselenite bis(hydrogenselenite) were synthesized and their crystal structures determined. Crystal data for $Ca(HSeO_3)_2 \cdot H_2O$: $a = 6.911(2)$, $b = 7.369(2)$, $c = 6.739(2)$ Å, $\alpha = 90.51(3)°$, $\beta = 90.93(3)°$, $\gamma = 107.46(2)°$, $V = 327.3(2)$ Å^3, space group $P\bar{1}$ (No. 2), $d_{calcd} = 3.19$ M gm^{-3}, $Z = 2$, and $R = 0.036$ for 1503 reflections. Data for $Ca_2(HSeO_3)_2(Se_2O_5)$: $a = 14.719(4)$, $b = 7.059(2)$, $c = 11.793(2)$ Å, $\beta = 117.96(2)°$, $V = 1082.3(4)$ Å^3, space group $C2/c$ (No. 15), $d_{calcd} = 3.52$ Mg m^{-3}, $Z = 4$, and $R = 0.047$ for 1251 reflections. Both structures form a three-dimensional network. The coordination polyhedron around calcium is a monocapped trigonal prism in dicalcium diselenite bis(hydrogenselenite) and a bicapped trigonal prism in calcium hydrogenselenite monohydrate. The Ca–O distance varies from 2.368 to 2.615 Å. Thermal behavior was investigated and the infrared spectrum assigned for dicalcium diselenite bis(Hydrogenselenite).

Introduction

Selenium(IV) forms the anions selenite SeO_3^{2-}, hydrogenselenite $HSeO_3^{1-}$, and diselenite $Se_2O_5^{2-}$, depending on the conditions in solution. Normal selenite crystallizes from neutral solution, diselenite from concentrated solution, and hydrogen selenite from acidic solution. In solution hydrogenselenite and diselenite are in equilibrium: $2HSeO_3^{2-} \rightleftharpoons Se_2O_5^{2-} + H_2O$. Diselenite is also formed from selenite and hydrogenselenite by heating.

Calcium forms a normal selenite $CaSeO_3 \cdot H_2O$ (*1*, *2*) and a diselenite $CaSe_2O_5$ (*3*). The diselenite has been synthesized by solid state reaction at 350°C. Finding no information about hydrogenselenites of calcium in the literature, we began an investigation leading to the synthesis and analysis of two compounds: calcium hydrogenselenite monohydrate $Ca(HSeO_3)_2 \cdot H_2O$ and dicalcium diselenite bis(hydrogenselenite) $Ca_2(HSeO_3)_2(Se_2O_5)$. Preparation, chemical analysis, IR spectrum, and thermal behavior of calcium hydrogenselenite monohydrate have been reported earlier (*1*).

This is not the first time that a compound with two different anions of selenium(IV) has been synthesized. Similar compounds have been reported for manganese and praseodymium (*12*, *13*).

Experimental

Preparation and analysis. Dicalcium diselenite bis(hydrogenselenite) was synthesized as follows: solid calcium carbonate

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was dissolved in 20% selenious acid such that the molar ratio of calcium and selenium was about 1 : 10. Colorless crystals formed during slow evaporation of the solution at 40°C.

Elemental analysis of calcium and selenium was carried out with a Perkin–Elmer 5000 atomic absorption spectrometer. Results were: Ca 13.5% and Se 55.0%. Calculated values for $Ca_2(HSeO_3)_2(Se_2O_5)$ were: Ca 13.96% and Se 55.02%.

Thermal analysis and IR spectrum. Thermal behavior was determined with a Perkin–Elmer Thermo Balance TG-2. Sample size was about 10 mg, heating rate 10°C/min, and air flow 50 cm^3/min.

The IR spectrum was recorded with a Perkin–Elmer 283 IR spectrometer. A KBr pellet was used with a scan time of 12 min and scan range from 4000 to 200 cm^{-1}.

Data collection and structure determination. Unit cell determination and intensity data collection were made with a Syntex $P2_1$ automatic single crystal diffractometer with graphite monochromatized Mo$K\alpha$ radiation. Unit cell dimensions were refined using least squares refinement. The space group was determined from systematic absences and intensity data were corrected for Lorentz and polarization effects and for absorption. The semiempirical absorption correction method was used with five different 2θ values. The largest measured relative reduction in intensity was from 1 to 0.49 for $Ca(HSeO_3)_2 \cdot H_2O$ and from 1 to 0.55 for $Ca_2(HSeO_3)_2(Se_2O_5)$. The results of the data collection are summarized in Table I.

Structures were solved by direct methods using the program MULTAN (*4*). Multan gave the sites of selenium and calcium atoms and oxygen atoms were found from a subsequent electron density map. No attempt was made to locate hydrogen atoms. Refinement of the structure and calculation of bond distances were made with the XRAY (*5*) program package and pictures were drawn with ORTEP, which is a part of the XRAY system.

Scattering factors for neutral atoms were those of Cromer and Mann (*6*) and refinement was based on structure factors and unit weights.

Results and Discussion

Thermal analyses

Thermal behavior of the two compounds is similar. First, hydrogenselenite decomposes to diselenite and water (reactions 1 and 2), and then diselenite forms normal selenite with liberation of selenium dioxide (reactions 3 and 4). There is an intermediate product of $Ca_2Se_3O_8$ between diselenite and normal selenite. In a final stage selenite decomposes to calcium oxide and selenium dioxide (reaction 5).

$$Ca_2(HSeO_3)_2(Se_2O_5) \rightarrow 2CaSe_2O_5 + H_2O \quad (1)$$

$$Ca(HSeO_3)_2 \cdot H_2O \rightarrow CaSe_2O_5 + 2H_2O \quad (2)$$

Subsequent reactions are similar for the two compounds:

$$2CaSe_2O_5 \rightarrow Ca_2Se_3O_8 + SeO_2 \quad (3)$$

$$Ca_2Se_3O_8 \rightarrow 2CaSeO_3 + SeO_2 \quad (4)$$

$$CaSeO_3 \rightarrow CaO + SeO_2 \quad (5)$$

Temperature ranges are 220–280°C for reaction 1, 120–260°C for reaction 2, 300–400°C for reaction 3, 410–500°C for reaction 4, and 980–1030°C for reaction 5. The observed thermal behaviour is in good agreement with the literature (*1, 7*).

The starting temperature of reaction 2 is low which indicates that water is weakly bonded to the structure. This was confirmed by crystal structure analysis.

IR Spectrum

IR spectra of the two compounds are listed in Table II. Assignments were made

TABLE I

SUMMARY OF CRYSTAL DATA AND DATA COLLECTION

Formula	$Ca(HSeO_3)_2 \cdot H_2O$	$Ca_2(HSeO_3)_2(Se_2O_5)$
Formula weight	314.03	574.01
a (Å)	6.911(2)	14.719(4)
b (Å)	7.369(2)	7.059(2)
c (Å)	6.739(2)	11.793(2)
α (°)	90.51 (3)	90
β (°)	90.93 (3)	117.96 (2)
γ (°)	107.46 (2)	90
V (Å^3)	327.30 (19)	1082.29 (43)
Space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
d_{calcd} (Mg m^{-3})	3.19	3.52
Z	2	4
μ (cm^{-1})	119.0	144.0
$F(000)$	296	1064
Crystal dimensions (mm)	0.1 × 0.2 × 0.3	0.3 × 0.4 × 0.4
Temperature (°C)	23 ± 1	23 ± 1
$\lambda(MoK\alpha)$ (Å)	0.7107	0.7107
Number of reflections used for measuring lattice parameters	15	15
Range of reflections used for measuring lattice parameters	5.80–14.21	20.53–30.21
Collection method	$\theta/2\theta$	$\theta/2\theta$
Scan speed (°/min)	3	3
Range of data collection (°)	5–60	5–65
Number of collected reflections	1924	2105
Number of refined independent reflections	1503 ($I > 4\delta(I)$)	1251 ($I > 3\delta(I)$)
R (ISO)	0.048	0.161
R (ANISO)	0.036	0.047
R_w (ANISO)	0.048	0.057

TABLE II

IR SPECTRA DATA (cm^{-1}) OF $Ca_2(HSeO_3)_2(Se_2O_5)$ AND $Ca(HSeO_3)_2 \cdot H_2O$

Assignment	$Ca_2(HSeO_3)_2(Se_2O_5)$	$Ca(HSeO_3)_2 \cdot H_2O$[a]
ν(O–H) (H_2O)	—	3236 b
ν(O–H) (SeOH)	2772 b 2376 m	2715 b 2320 m
δ(H–O–H) (H_2O)	—	1670
δ(Se–O–H) (SeOH)	1250 s	1205 m 1251 m
ν_s(Se–O)	856 vs	867 s
ν_{As}(Se–O)	823 vs	808 vs
ν(Se–O) (SeOH)	666 sh 618 vs	638 vs
ν(Se–O) (Se–O–Se)	536 s	—
δ(O–Se–O)	450 s	465 vs
δ(O–Se–OH)	382 s 318 m	389 w 323 m

[a] From Ref. (*1*), vs = very strong, s = strong, m = medium, sh = shoulder, b = broad, w = weak.

TABLE III

Fractional Coordinates with Estimated Standard Deviations in Parentheses and Temperature Factor U_{eq} (U_{eq} = 100*($U11$ + $U22$ + $U33$)/3) for $Ca(HSeO_3)_2 \cdot H_2O$

Atom	x	y	z	U_{eq}
Se(1)	.74841(2)	−.03727(2)	.34243(2)	.96
Se(2)	.81965(2)	.59264(2)	.86831(2)	1.02
Ca(1)	.77174(5)	.07785(4)	.87837(4)	.87
O(1)	.95759(17)	.04504(18)	.21104(18)	1.64
O(2)	.58540(17)	.01975(18)	.19172(16)	1.53
O(3)	.78435(20)	.14391(19)	.52888(17)	1.97
O(4)	.91911(18)	.65041(18)	.09572(18)	1.56
O(5)	.64318(17)	.71534(17)	.85624(18)	1.62
O(6)	.65651(20)	.36270(18)	.90111(20)	2.01
O(7)	.29716(26)	.55745(23)	.59145(21)	3.47

TABLE IV

Fractional Coordinates with Estimated Standard Deviations in Parentheses and Temperature Factor U_{eq} (U_{eq} = 100*($U11$ + $U22$ + $U33$)/3) for $Ca_2(HSeO_3)_2(Se_2O_5)$

Atom	x	y	z	U_{eq}
Se(1)	.2823(1)	.3629(1)	.1606(1)	1.40
Se(2)	.0901(1)	.2643(1)	.3937(2)	6.72
Ca(1)	.9795(1)	.2488(2)	.5749(2)	1.32
O(1)	.3950(5)	.2501(11)	.2061(7)	2.47
O(2)	.2846(7)	.3647(11)	.3122(7)	4.39
O(3)	.1926(5)	.1969(9)	.0877(6)	1.84
O(4)	.0778(6)	.4317(9)	.4830(7)	2.88
O(5)	.0253(6)	.0899(9)	.4126(7)	2.80
O(6)[a]	.0419(14)	.3609(25)	.2572(15)	4.81

[a] Population parameter 0.5.

according to the literature (*1, 8*). Both compounds contain typical Se–O stretching and O–Se–O bending, and also Se–OH stretching and O–Se–OH bending vibrations. The main differences in the spectra are the vibrations of crystal water in calcium hydrogenselenite monohydrate and the Se–O stretching of the bridge oxygen in the diselenite group.

Crystal Structure

Fractional coordinates are listed in Tables III and IV[1] and interatomic distances in Tables V and VI.

The selenite group SeO_3 forms a trigonal prism with three oxygen atoms and one selenium atom at the apexes. The normal selenium–oxygen distance is about 1.67 Å. In the case of hydrogenselenite a hydrogen atom is connected to one of the oxygen atoms causing elongation of the selenium–oxygen distance.

The phenomenon is seen in both compounds: in calcium hydrogenselenite monohydrate the Se1–O3 and Se2–O6 distances are elongated and in dicalcium diselenite bis(hydrogenselenite) the Se1–O2 distance is elongated.

The diselenite group Se_2O_5 is formed from two selenite groups, which have a common oxygen atom as a bridge between

TABLE V

Interatomic Distances (Å) and Angles (°) around Selenium Atoms

	$Ca(HSeO_3)_2 \cdot H_2O$	$Ca_2(HSeO_3)_2(Se_2O_5)$
Se1–O1	1.663(1)	1.686(7)
Se1–O2	1.653(1)	1.773(10)
Se1–O3	1.784(1)	1.671(6)
Se2–O4	1.668(1)	1.649(8)
Se2–O5	1.724(1)	1.636(8)
Se2–O6	1.749(1)	1.744(8)[a]
O1–Se1–O2	99.11 (6)	97.5 (4)
O1–Se1–O3	101.47 (6)	104.8 (3)
O2–Se1–O3	100.56 (6)	99.3 (4)
O4–Se2–O5	101.84 (6)	101.9 (5)
O4–Se2–O6	102.20 (6)	93.7 (5)[a]
O5–Se2–O6	99.34 (6)	102.5 (5)[a]
Se2–O6–Se2	—	131.3 (1.2)[a]

[a] O6 in special position 0, 0.3609, 1/4.

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[1] See NAPS Document No. 04407 for 22 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

TABLE VI

INTERATOMIC DISTANCES (Å) AROUND Ca ATOM

$Ca(HSeO_3)_2 \cdot 2H_2O$		$Ca_2(HSeO_3)_2(Se_2O_5)$	
Ca–O1	2.615(1)	Ca–O1	2.368(6)
–O1	2.393(1)	–O1	2.398(9)
–O2	2.465(1)	–O3	2.382(5)
–O2	2.392(1)	–O4	2.530(9)
–O3	2.407(1)	–O4	2.393(7)
–O4	2.454(1)	–O5	2.566(9)
–O5	2.552(1)	–O5	2.399(7)
–O6	2.463(1)		

two selenium atoms. This bridged selenium–oxygen distance is always elongated, as in dicalcium diselenite bis(hydrogenselenite) the distance between Se2 and O6. Oxygen atom O6 should be in special position $0,y,\frac{1}{4}$, but refinement gave too high temperature factors, indicating that it must be disordered. Oxygen atom O6 was accordingly refined in position 0.042, 0.361, 0.257 with the population parameter 0.5.

The usual coordination numbers for calcium vary from five to nine and in the present compounds the coordination numbers are seven and eight (Table VI). Common coordination polyhedra for eight coordination are dodecahedron, square antiprism, and bicapped trigonal prism, but cubic, hexagonal bipyramid, and bicapped trigonal antiprism are also possible. Three important polyhedra for seven coordination are monocapped octahedron, pentagonal bipyramid, and monocapped trigonal prism. Calcium hydrogenselenite monohydrate proved to be one of those compounds for which it is difficult to select the right polyhedron and therefore, assistance was saught from the δ-test of Porai-Koshits and Aslanov (*9–11*).

The polyhedron around the calcium atom in dicalcium diselenite bis(hydrogenselenite) is clearly a monocapped trigonal prism as shown in Fig. 1, and the δ-test (Table VII) supports this conclusion.

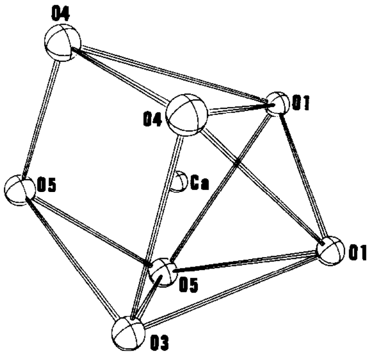

FIG. 1. Coordination polyhedron around calcium in dicalcium diselenite bis(hydrogenselenite).

The coordination polyhedron around calcium in calcium hydrogenselenite monohydrate is either a distorted square antiprism or a distorted bicapped trigonal prism (Fig. 2). If the polyhedron is thought to be a square antiprism, the oxygen atoms O6, O4, O1, and O2 form the upper square and the oxygen atoms O5, O1, O3, and O2 the lower square, as shown in Fig. 2. But the polyhedron can also be interpreted as a bicapped trigonal prism, in which case the oxygen atoms O1, O1, and O4 form one end triangle and the oxygenatoms O2, O2, and O6 the other with the atoms O5 and O3 as capping atoms. The δ-test (see Table VII)

TABLE VII

δ-TEST FOR COORDINATION POLYHEDRON AROUND CALCIUM

	δ_1	δ_2	δ_3	δ_4
Dodecahedron	29.5°	29.5°	29.5°	29.5°
Square antiprism	0.0°	0.0°	52.4°	52.4°
Bicapped trigonal prism	0.0°	21.8°	48.2°	48.2°
$Ca(HSeO_3)_2 \cdot H_2O$	7.7°	36.6°	44.2°	51.6°
Capped octahedron	24.2°	24.2°	24.2°	—
Pentagonal bipyramid	54.4°	54.4°	—	—
Monocapped trigonal prism	0.0°	0.0°	41.5°	—
$Ca_2(HSeO_3)_2(Se_2O_5)$	6.6°	23.2°	54.4°	—

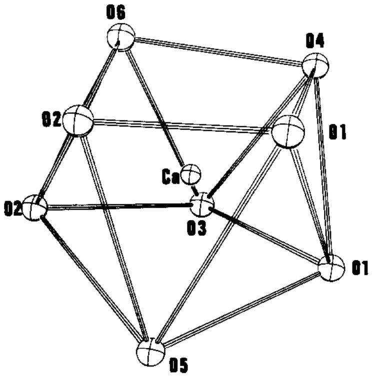

FIG. 2. Coordination polyhedron around calcium in calcium hydrogenselenite monohydrate.

does not resolve the geometry, but the theoretical values of the bicapped trigonal prism are closer than the values of the square antiprism to those calculated for calcium hydrogenselenite monohydrate, and for that reason we judged the coordination polyhedron around calcium to be bicapped trigonal prism.

The structure of dicalcium diselenite bis(hydrogenselenite) is complicated because both the diselenite group and the hydrogenselenite group form bridges between calcium atoms. The structure is a three-dimensional network. The hydrogenselenite group connects three calcium atoms: O1 is connected to two calcium atoms and O3 to one calcium atom. The hydrogen atom of hydrogenselenite is bonded to O2 since Se1–O2 distance is elongated. And probably it forms a hydrogen bond O2–H···O3 between atoms O2 and O3 with a distance 2.58 Å, where O3 belongs to the other selenite group. The diselenite group connects eight calcium atoms, as each of the O4 and O5 atoms is connected to different calcium atoms. Oxygen atom O6 is not connected to calcium but forms a bridge between two selenium atoms. A drawing of the packing is shown in Fig. 3.

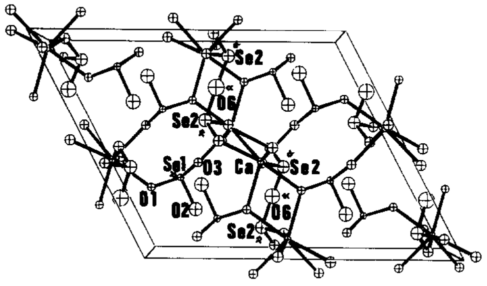

FIG. 3. The structure of dicalcium diselenite bis(hydrogenselenite) along the *b*-axis.

The structure of calcium hydrogenselenite monohydrate is also a three-dimensional network, but less complicated than the previous structure. It can be thought to consist of chains connected together (see Fig. 4). Selenite groups are not identical: the Se1 group connects five calcium atoms and the Se2 group connects three. The site of the hydrogen atom in the first hydrogenselenite group is clear; it is connected to oxygen atom O3 as indicated by the elongated selenium distance of 1.784 Å. In the second selenite group there are two possible elongated selenium–oxygen distances, but since Se2–O6 is slightly longer it can be assumed that hydrogen is connected to this atom. There is also one uncoordinated oxygen atom (O7) in calcium hydrogenselenite monohydrate. It is located in a hole in the structure so that there are only three oxygen atoms (O3, O4, O5) at a distance less

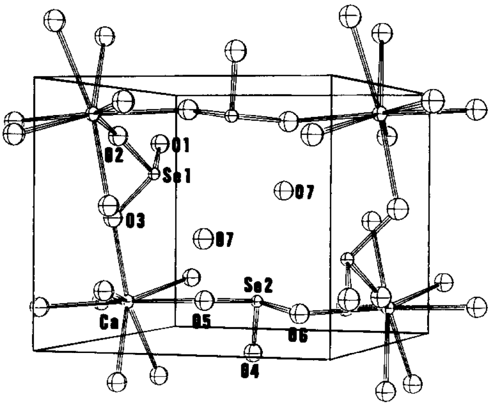

FIG. 4. The structure of calcium hydrogenselenite monohydrate along the *a*-axis.

TABLE VIII

AVERAGE Se–O AND Ca–O DISTANCES (Å) IN CALCIUM SELENITES AND COORDINATION NUMBER AROUND Ca ATOM

	Se–O	Se–O(–H)	Se–O(–Se)	Ca–O	CN	Ref.
$CaSeO_3 \cdot H_2O$	1.69	—	—	2.42	7	2
$CaSe_2O_5$	1.66	—	1.83	2.43	7	3
$Ca_2(HSeO_3)_2(Se_2O_5)$	1.66	1.77	1.74	2.43	7	—[a]
$Ca(HSeO_3)_2 \cdot H_2O$	1.68	1.77	—	2.47	8	—[a]

[a] This work.

than 3.0 Å. The oxygen atom O7 is most likely connected to the structure by hydrogen bonds, probably through the oxygen atoms O3 and O4, since the O7–O3 distance of 2.565 Å and O7–O4 distance of 2.795 are suitable for hydrogen bonds.

Bond distances in calcium compounds formed by selenium(IV) oxoacids are summarized in Table VIII. The average Se–O distance is 1.67 Å. When the compound is a hydrogen selenite, one Se–O distance is elongated to the average distance 1.77 Å. In the diselenites, the Se–O(–Se) distance is elongated. The calcium–oxygen distances are almost identical, except in calcium hydrogenselenite monohydrate, where the distance is slightly greater because of the larger coordination number.

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