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Gallium Hydrogen Selenite Diselenite Hydrate, $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$: A Novel Structure Type Containing Alternating Cationic and Anionic Layers

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$Ga(HSeO_3)(Se_2O_5).1.07H_2O$ ($P2_1/a$, a = 9.0648(8) Å, b = 6.5118(4) Å, c = 14.323(1) Å, β = 105.91(3)°, Z = 4, V = 813.1 Å^3) was prepared hydrothermally in a steel autoclave at 200 °C. The structure was solved using room-temperature single-crystal X-ray diffraction data from 2398 observed reflections ($I > 3\sigma(I)$), R = 3.68%, R_w = 5.34%. $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$ has a double-layered type structure, with positively charged layers containing the $HSeO_3$ units alternating with negatively charged ones containing the Se_2O_5 groups.

Introduction

The selenite anion has been shown to be a versatile ligand in selenium(IV) oxo compounds: for example, depending on the synthesis conditions, crystalline solids containing selenite, SeO_3^{2-}, hydrogen selenite, SeO_3H^-, and diselenite, $Se_2O_5^{2-}$, anions can be prepared. Selenite-containing materials are most easily prepared in approximately neutral reaction conditions; thus, $Al_2(SeO_3)_3\cdot 3H_2O$[1] and $Al_2(SeO_3)_3\cdot 6H_2O$[2] are both made hydrothermally at pH 7, but at temperatures of 200 and 70 °C, respectively. Hydrogen selenites are synthesised using slightly more acidic conditions; e.g., $AlHSe_2O_6\cdot 2H_2O$[2] and $InHSe_2O_6$[3] are both produced at ~pH 3 using excess selenious acid in the reaction mixtures. The use of even higher concentrations of H_2SeO_3 in the starting mixture can produce diselenite containing compounds, and there are a number of examples of this type among selenites of divalent transition metals, e.g., $ZnSe_2O_5$,[4] $MnSe_2O_5$,[5] and $CuSe_2O_5$.[6] Previous studies of the group IIIB metal selenites, however, have failed to produce a material where the selenium(IV) atom is part of a diselenite ligand. This paper describes the synthesis and characterization of $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$, in which both hydrogen selenite and diselenite ions are present in an alternating anionic/cationic layer structure. The only other example of a mixed hydrogen selenite/diselenite compound is $PrH_3(SeO_3)_2(Se_2O_5)$.[7] Other selenites of the group IIIB metals that have been characterized by single-crystal diffraction methods include $Ga_2(SeO_3)_3\cdot 3H_2O$,[8] which is isostructural with the corresponding aluminum compound,[1] and $CsGa_2H(SeO_3)_4\cdot 2H_2O$[9] and $Cs_3In_2H_6(SeO_3)_{12}$.[10] A number of other materials have been tentatively characterized by means of their infrared spectra.[11,12]

Experimental Section

$Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$ was prepared from a solution of $GaCl_3$ in water (1 M), to which a large excess of selenious acid (2 M) had been added. The reaction mixture (15 mL) was placed in a 25-mL capacity Teflon-lined steel autoclave, heated to 200 °C for 2 days, and then left to cool. Colorless, platelike crystals were recovered from the bomb by suction filtration and dried in air.

A suitable crystal for structure determination (0.4 × 0.3 × 0.04 mm) was mounted on a Huber four-circle diffractometer and room-temperature X-ray data were collected (graphite-monochromated Mo Kα, λ = 0.710 69Å) as outlined in Table I. The monoclinic cell constants were determined from the positions of 25 centered reflections and optimized by least-squares refinement; the resulting lattice parameters are shown in Table I. Data were collected in the ω–2θ scanning mode. Three standard reflections were monitored during the course of the experiment and these showed no significant intensity variation. The scan speed was 6° min^{-1} with a scan range from 1.3° below Kα_1 to 1.6° above Kα_2. Ψ-scans for three reflections were used to correct for crystal absorption. The raw data were reduced using a Lehmann–Larsen profile fitting routine and the normal corrections for Lorentz and polarization effects were applied. All the data collection and reduction routines were based on the UCLA package.[13]

The systematic absences allowed the space group to be unambiguously assigned as $P2_1/a$ (No. 14). The selenium and gallium atom positions were located using the direct methods program SHELXS86,[14] and subsequent difference Fourier syntheses revealed the locations of the oxygen atoms. Thermogravimetric analysis showed that approximately 1 molecule of water was lost per gallium atom during thermal decomposition (observed weight loss ~4% at approximately 170 °C; calculated weight loss 3.9%). Only one water molecule oxygen could be refined satisfactorily, although the largest peak in a final difference Fourier map, centered at (0,0.5,0.5), could be refined as the oxygen (O(10)) of a second water molecule, with a fractional occupation factor of 0.15(1). This leads to the final composition of the compound being postulated as approximately $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$. The remaining peaks in the final Fourier synthesis were too close to the selenium atom positions, and could not be refined as extra water molecule oxygens. For the final

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Table I. Data Collection and Refinement Details for $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$

formula weight	454.8
Crystal Data	
crystal system	monoclinic
a/Å	9.0648(8)
b/Å	6.5118(4)
c/Å	14.323(1)
β/deg	105.91(3)
V/Å^3	813.1
space group	$P2_1/a$
D_c/g cm^{-1}	3.72
$F(000)$	823
Z	4
linear abs coeff/cm^{-1}	166.9
Data Collection	
X-radiation	Mo Kα
2θ min, max/deg	1, 65
obsd data	2398
$[I > n\sigma(I)]$, n =	3
abs corr/min, max	1.00, 2.51
Refinement	
no. of parameters	128
$\Delta\rho$(max)/e Å^{-3}	2.9
final R/%^{a}	3.68
final R_w/%^{a}	5.34

^{a} $R = \sum_h|(|F_o| - |F_c|)|/\sum_h|F_o|$, $R_w = \sqrt{\sum_h w_h(|F_o|^2 - |F_c|^2)/\sum w_h|F_o|^2}$.

cycle of least-squares refinement against F, anisotropic temperature factors were included for the Se, Ga, and O atoms (except O(10)). The final weighting scheme was that of Tukey and Prince, fitted using a truncated Chebyshev polynomial (coefficients 12.294, −2.445, 6.782).

All least-squares, Fourier, and subsidiary calculations were carried out using the Oxford CRYSTALS system,[15] running on a DEC Microvax 3200 computer. Complex neutral atom scattering factors were obtained from ref 16.

Discussion

The structure of $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$ (Figure 1) is double layered, consisting of alternating $[Ga_{0.5}(HSeO_3)\cdot H_2O]_n{}^{n/2+}$ and $[Ga_{0.5}(Se_2O_5)]_n{}^{n/2-}$ layers stacked along the c direction, with the remaining water molecules in spaces in the $Ga_{0.5}(HSeO_3)\cdot H_2O$ layers. This is the first such alternating cationic/anionic layer selenite material to be discovered and joins a small class of inorganic compounds with this structural feature; these include the chlorite minerals[17] and $[Na_4Mg_2Cl_{12}][Mg_7Al_4(OH)_{22}]$.[18] Neither of these two structure types show any relationship to the structure reported here. The diselenite group, containing Se(1) and Se(2), shows a similar coordination geometry to other diselenite groups that have been reported in the literature,[19,20] the Se–O bridging bonds being markedly longer than the other Se–O bonds in the ion. The hydrogen selenite groups show the expected coordination of selenium by oxygen; a slightly distorted trigonal pyramid, with the Se–OH bond marginally longer than the other Se–O bonds. The gallium atoms are both coordinated in an almost regular octahedral fashion by oxygen. The atomic coordinates, bond distances, and bond angles are given in Tables II–IV, respectively.

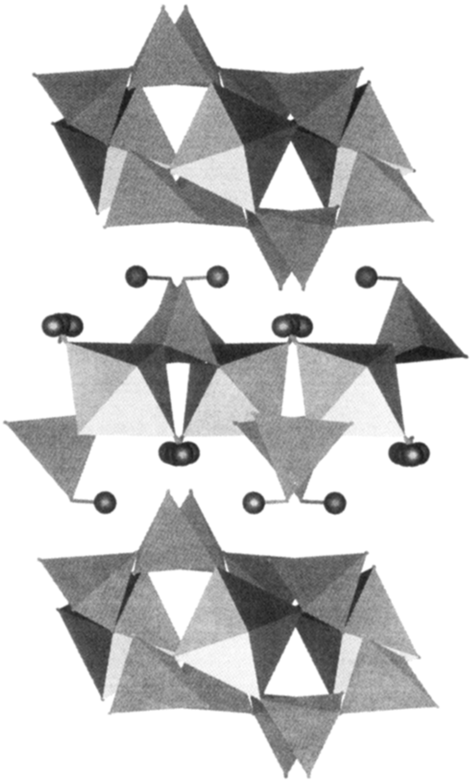

Figure 1. Structure of $Ga(HSeO_3)(Se_2O_5)\cdot 1\cdot 07H_2O$ viewed parallel to the [100] direction clearly showing the alternating cationic/anionic layered nature of the material. Illustrated are Ga-centered octahedra and the selenite trigonal pyramids; hydrogen atoms are shown as spheres.

Table II. Final Atomic Coordinates and Equivalent Isotropic Temperature Factors for $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$

atom	x	y	z	$U_{equ}{}^a$/Å^2
Se(1)	0.15774(8)	0.1600(1)	0.90253(5)	0.0144
Se(2)	0.88674(8)	0.8343(1)	0.82730(5)	0.0143
Se(3)	0.76977(8)	0.2017(1)	0.60611(5)	0.0151
Ga(1)	0.0000	0.5000	0.0000	0.0135
Ga(2)	0.0000	0.0000	0.5000	0.0148
O(1)	0.9857(6)	0.7838(8)	0.0480(4)	0.0163
O(2)	0.7159(6)	0.9556(8)	1.0035(4)	0.0181
O(3)^b	0.4674(6)	0.2649(9)	0.4016(4)	0.0212
O(4)	0.4427(7)	0.9065(8)	0.8635(4)	0.0180
O(5)	0.0530(6)	0.8123(8)	0.4061(4)	0.0164
O(6)	0.1830(8)	0.718(1)	0.2712(4)	0.0253
O(7)	0.8292(7)	0.799(1)	0.7083(4)	0.0214
O(8)	0.4225(6)	0.436(1)	0.1654(4)	0.0205
O(9)	0.2151(6)	0.0714(9)	0.5485(4)	0.0195
O(10)^b	0.0000	0.5000	0.5000	0.011(7)^{fl}
H(1)	0.13(2)	0.58(2)	0.27(1)	0.05^c
H(2)	0.37(2)	0.22(2)	0.37(1)	0.05^c
H(3)	0.52(2)	0.26(2)	0.38(1)	0.05^c

^{a} $U_{equ} = (U_1U_2U_3)^{1/3}$ where U_i are the root-mean-square deviations along the principal axes of the thermal ellipsoids. ^{b} Oxygen atoms of water molecules. Fractional occupation factor for O(10) is 0.15(1). ^{fl}U_{iso}. ^{c} Not refined.

The $Ga_{0.5}(Se_2O_5)$ layer (see Figure 2) consists of Se_2O_5 groups which link three gallium-centered octahedra via O(1), O(2), and O(4) into a puckered layer parallel to the ab plane. No two oxygens of a diselenite groups are bound to the same gallium atom. O(8) is the bridging oxygen of the diselenite group and O(7) is a hanging oxygen involved in hydrogen bonding. The $Ga_{0.5}(HSeO_3)\cdot H_2O$ layer (Figure 3) also consists of isolated GaO_6 octahedra, linked via the sharing of hydrogen selenite vertices into a flat sheet. Each $HSeO_3$ unit shares two vertices, O(5) and O(9) with two

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Table III. Selected Bond Distances (Å) for $Ga(HSeO_3)(Se_2O)_5\cdot 1.07H_2O$

Se(1)–O(1^a)	1.683(5)	Se(1)–O(2^b)	1.687(5)
Se(1)–O(8^c)	1.794(6)		
Se(2)–O(4^n)	1.686(5)	Se(2)–O(7^k)	1.657(5)
Se(2)–O(8^e)	1.828(5)		
Se(3)–O(5^a)	1.666(5)	Se(3)–O(6^a)	1.770(6)
Se(3)–O(9^o)	1.699(6)		
Ga(1)–O(1^g)	1.988(5)	Ga(1)–O(1^h)	1.988(5)
Ga(1)–O(2^c)	1.966(5)	Ga(1)–O(2^i)	1.966(5)
Ga(1)–O(4^c)	1.976(5)	Ga(1)–O(4^i)	1.976(5)
Ga(2)–O(3^c)	2.046(5)	Ga(2)–O(3^d)	2.046(5)
Ga(2)–O(5^j)	1.972(5)	Ga(2)–O(5^f)	1.972(5)
Ga(2)–O(9^k)	1.939(5)	Ga(2)–O(9^l)	1.939(5)
O(6)–H(1^m)	0.9(1)	O(3)–H(2^k)	0.9(1)
O(3)–H(3^k)	0.8(1)		

[a] $1-x, 1-y, 1-z$. [b] $1-x, 1-y, 2-z$. [c] $1/2-x, y-1/2, 1-z$. [d] $x-3/2, -y-1/2, z$. [e] $3/2-x, y+1/2, 1-z$. [f] $-x, 1-y, 1-z$. [g] $x-1, y, z$. [h] $1-x, 1-y, 1-z$. [i] $x-3/2, 1/2-y, z-1$. [j] $x, y-1, z$. [k] x, y, z. [l] $-x, -y, 1-z$. [m] $1/2-x, y+1/2, 1-z$. [n] $1/2-x, 1/2-y, z$. [o] $1/2-x, -1/2-y, z$.

Table IV. Selected Bond Angles (deg) for $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$

O(2^b)–Se(1)–O(1^a)	101.2(3)	O(8^c)–Se(1)–O(1^a)	99.2(2)
O(8^c)–Se(1)–O(2^b)	99.0(3)		
O(7^k)–Se(2)–O(4^n)	99.8(3)	O(8^e)–Se(2)–O(4^n)	96.8(3)
O(8^e)–Se(2)–O(7^k)	97.7(3)	Se(1^m)–O(8)–Se(2^m)	124.2(2)
O(6^a)–Se(3)–O(5^a)	98.2(3)	O(9^o)–Se(3)–O(5^a)	99.1(3)
O(9^o)–Se(3)–O(6^a)	100.6(3)		
O(1^h)–Ga(1)–O(1^g)	179.99	O(2^c)–Ga(1)–O(1^g)	89.2(2)
O(2^i)–Ga(1)–O(1^h)	89.2(2)	O(2^c)–Ga(1)–O(1^h)	90.8(2)
O(2^i)–Ga(1)–O(1^g)	90.8(2)	O(2^c)–Ga(1)–O(2^i)	179.99
O(4^c)–Ga(1)–O(1^h)	91.8(2)	O(4^c)–Ga(1)–O(1^g)	88.2(2)
O(4^c)–Ga(1)–O(2^i)	91.7(2)	O(4^c)–Ga(1)–O(2^c)	88.3(2)
O(4^i)–Ga(1)–O(1^g)	91.8(2)	O(4^i)–Ga(1)–O(1^h)	88.2(2)
O(4^i)–Ga(1)–O(2^c)	91.7(2)	O(4^i)–Ga(1)–O(2^i)	88.3(2)
O(4^c)–Ga(1)–O(4^i)	179.99		
O(3^d)–Ga(2)–O(3^f)	179.99	O(5^i)–Ga(2)–O(3^f)	89.4(2)
O(5^f)–Ga(2)–O(3^d)	89.4(2)	O(5^f)–Ga(2)–O(3^f)	90.6(2)
O(5^i)–Ga(2)–O(3^d)	90.6(2)	O(5^f)–Ga(2)–O(5^i)	179.99
O(9^l)–Ga(2)–O(3^f)	90.5(2)	O(9^k)–Ga(2)–O(3^f)	89.5(2)
O(9^k)–Ga(2)–O(3^d)	90.5(2)	O(9^l)–Ga(2)–O(3^d)	89.5(2)
O(9^l)–Ga(2)–O(5^i)	90.9(2)	O(9^k)–Ga(2)–O(5^j)	89.1(2)
O(9^k)–Ga(2)–O(5^f)	90.9(2)	O(9^l)–Ga(2)–O(5^f)	89.1(2)
O(9^k)–Ga(2)–O(9^l)	179.99		

[a] $1-x, 1-y, 1-z$. [b] $1-x, 1-y, 2-z$. [c] $1/2-x, y-1/2, 1-z$. [d] $x-3/2, -y-1/2, z$. [e] $3/2-x, y+1/2, 1-z$. [f] $-x, 1-y, 1-z$. [g] $x-1, y, z$. [h] $1-x, 1-y, 1-z$. [i] $x-3/2, 1/2-y, z-1$. [j] $x, y-1, z$. [k] x, y, z. [l] $-x, -y, 1-z$. [m] $1/2-x, y+1/2, 1-z$. [n] $1/2-x, 1/2-y, z$. [o] $1/2-x, -1/2-y, z$.

gallium atoms, while the other oxygen, O(6), is protonated and points into the interlamellar region where it is presumably involved in hydrogen bonding. The GaO_6 octahedral units consist of two water molecules, which occupy the axial positions of the octahedron, plus oxygen atoms from four selenite groups which occupy the equatorial positions. The layers are linked in a way that produces holes big enough to contain extra water molecules.

The hydrogen bonding in the structure is fairly complex. Three of the five hydrogens in the structure were placed using geometric considerations and their atomic positions were refined successfully. The gallium-coordinated water molecule, containing O(3), H(2), and H(3), takes part in interlayer hydrogen bonding with two hanging O(7) atoms of the diselenite groups. The hydrogen selenite proton, H(1), is connected to O(6) and is involved in an interlayer hydrogen bond to O(4). The protons of the final water molecule, O(10), could not be placed with any degree of certainty. However, because the O(10) end of the polar water molecule is positioned inside the positive $Ga_{0.5}(HSeO_3)\cdot H_2O$ layer, it seems most likely that the $\delta+$ hydrogen ends will be oriented toward the negative $Ga_{0.5}(Se_2O_5)$ layer.

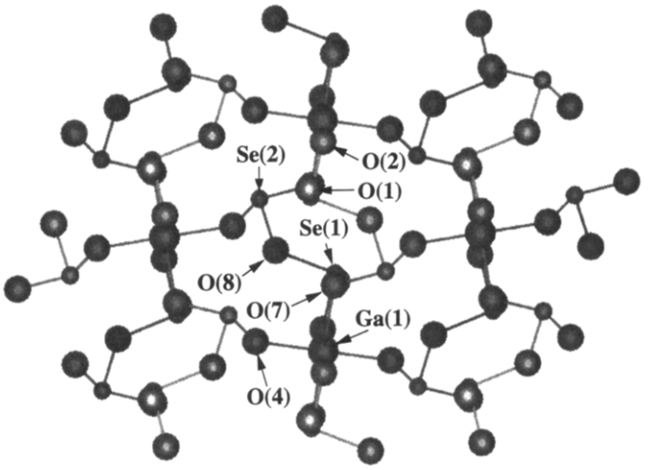

Figure 2. Details of the $Ga_{0.5}(Se_2O_5)$ layer, viewed along [001].

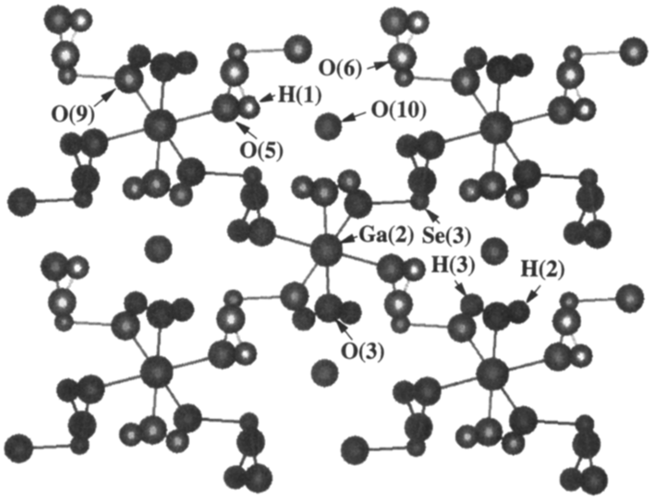

Figure 3. Details of the $Ga_{0.5}(HSeO_3)\cdot H_2O$ layer, viewed along [001].

Table V. Band Maxima (cm^{-1}) and Assignments for $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$

3000	$\nu(H_2O)$	720^a	$\nu_3(SeO_3)$
1380	$\delta(OH)$	770	$\nu_3(SeO_3)$
1151	$\delta(SeO_2OH)$	800^a	$\nu_3(SeO_3)$
990	$\delta(SeOSe)$	820^a	$\nu_1(SeO_3)$

[a] Shoulders.

Bond valence calculations carried out on the structure, including terms to account for the hydrogen bonds,[21] show that all the atoms have chemically reasonable bond valence values.

The infrared spectrum of $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$ shows a complicated band structure in the selenite ion stretching region due to the presence of two types of ion, diselenite and hydrogen selenite. The Se–O–Se δ band is seen at 990 cm^{-1}, the low-energy (400–600 cm^{-1}) region shows a number of bands that cannot be unambiguously assigned. Other assignments, made by comparison with other spectra of selenite species, are given in Table V.[5,6]

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Supplementary Material Available: List of thermal parameters for $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$ (1 page); list of observed and calculated structure factors for $Ga(HSeO_3)(Se_2O_5)\cdot 1.07H_2O$ (15 pages). Ordering information is given on any current masthead page.