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An Unusual Hydrogen Bonding Network in the Layered $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ Compound

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The layered compound $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ has been prepared hydrothermally (210°C, 22,000 psi). The structure contains alternating layers of $[Se_4]^{2-}$ ions and $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ sheets stacked along the c axis of the unit cell. The $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ layers comprise $^1_\infty[Ba(OH)(H_2O)_2(H_2O)_{6/2}]^+$ chains that are cross-linked to form nine-coordinate Ba^{2+} ions with four *inter*chain O–H ··· O hydrogen bonding interactions with O ··· O separations of 2.65–2.77 Å. The $[Se_4]^{2-}$ ions are hydrogen bonded to the $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ layers by virtue of five O–H ··· Se hydrogen bonding interactions with O ··· Se contacts of 3.44–3.62 Å. The latter are rare examples of hydrogen bonds to selenium. Crystal data: triclinic, space group $P\bar{1}$, $a = 6.0690(4)$, $b = 8.2956(5)$, $c = 9.8676(8)$ Å; $\alpha = 75.568(6)$, $\beta = 73.667(6)$, $\gamma = 71.438(6)°$; $V = 444.93(6)$ Å^3, $Z = 1$, $R = 0.0261$, $R_w = 0.0305$.

INTRODUCTION

Hydrogen bonding plays an important role in the structure and bonding of a variety of biological, organic, and inorganic compounds. Most of the hydrogen bonding observed in nature involves oxygen, nitrogen, or the halogens and is observed less frequently with the less electronegative heavier main-group elements (1). This tendency is consistent with the decrease in Brønsted basicity (and electronegativity) of the p-block elements as one moves down a group (2). Although hydrogen bonds are weaker in this region, they presumably play an important structural role in many systems. For example, hydrogen bonding to sulfur has been well established in cysteine-containing electron-transfer proteins (3, 4) and related inorganic model compounds (5, 6). Although hydrogen bonding to selenium is quite rare, Krebs and co-workers have reported a few examples of intermolecular O–H ··· Se interactions in the hydrated selenogermanides and selenostannides $Na_4Ge_2Se_6 \cdot 16H_2O$, $Na_4GeSe_4 \cdot 14H_2O$, and $Na_4SnSe_4 \cdot 16H_2O$ (7–9). The first *intra*molecular C–H ··· Se interactions, $d_{Se\cdots H} = 2.86$, 2.92 Å were only recently observed crystallographically (10).

We are interested in the preparation and characterization of new transition metal complexes containing heavier main-group ligands in both aqueous and nonaqueous environments. Hydrogen bonding interactions are occasionally encountered in these systems but usually do not significantly influence the structural properties (11). As part of our investigations, we have been interested in the preparation of mixed oxyselenide and oxytelluride transition metal complexes prepared in various media (12, 13). During the course of one of our reactions, we isolated a metal-free polyselenide with an unusual three-dimensional structure. Herein we described the synthesis and structure of $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ containing O–H ··· O and O–H ··· Se interactions in the solid state. The latter seem to play an important role in stabilizing the layered structure observed for this compound and are rare examples of hydrogen bonds to selenium.

EXPERIMENTAL

Synthesis and Characterization

The Ba–Se complex was isolated from a reaction between Nb, BaSe, Se, and H_2O (1 : 1 : 2 : 52 molar ratio) that was heated to 210°C and 22,000 psi in a LECO hydrothermal reactor for 72 hr. The reaction was conducted in a sealed Teflon bag that was loaded in an oxygen-free N_2 glove box. The pH of the solutions before and after reaction was between 10 and 11. Metallic plate-like products were isolated in the glovebox and washed with H_2O. The compound was characterized by energy dispersive X-ray

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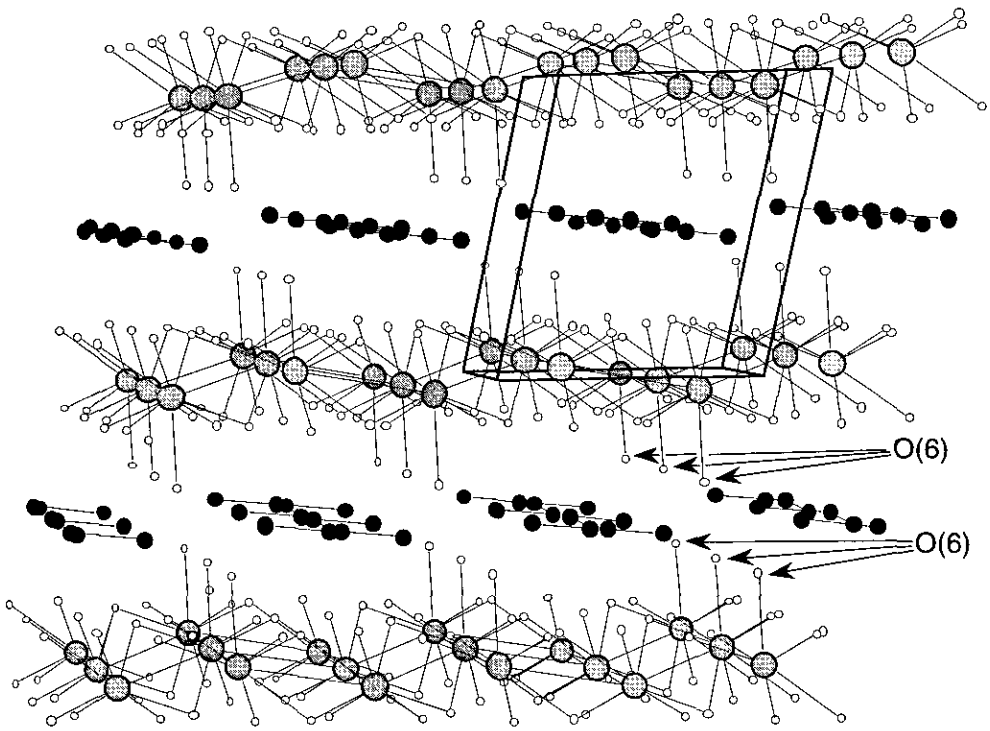

FIG. 1. An approximate (010) projection of the $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ structure showing the layered nature of the lattice. The Se atoms are black, the Ba atoms gray, and the O atoms white. The box represents the unit cell.

TABLE 1
Crystallographic Data for $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$

Empirical formula: $Ba_2H_{22}O_{12}Se_4$

Color Gray
Shape Block
Crystal dimensions (mm) 0.22 × 0.28 × 0.41
Space group $P\bar{1}$
Cell dimensions (25°C)
a = 6.0690(4) Å α = 75.568(6)°
b = 8.2956(5) Å β = 73.667(6)°
c = 9.8676(8) Å γ = 71.438(6)°
V = 444.93(6) Å^3
λ = 0.71073 Å
Z = 1
M = 804.69 g mole^{-1}
D_c = 3.003 g cm^{-3}
μ = 125.42 cm^{-1}
$F(000)$ = 366 e^-
2θ scan range = 2–60°
No. of individual reflections 2580
No. of individual observed reflections ($F_0 > 6\sigma(F_0)$) 2292
No. of parameters 82
R = 0.0261, R_w = 0.0305
S = 1.17
Max $\sigma/\Delta < 0.01$

analysis (EDX) and single crystal X-ray diffraction. The same results were obtained under the conditions of 245°C, 25,000 psi, and 90 hr. We were unsuccessful in preparing the crystalline compound in the absence of Nb metal. The fate of the Nb is unknown at present and Nb-containing products were not detected in the bulk products.

Powder X-ray diffraction (XRD) analysis of the bulk polycrystalline product mixtures revealed a preponderance of elemental Se and minor amounts (~ 10%) of the $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ product. The product was identi-

TABLE 2
Fractional Coordinates and Isotropic Thermal Parameters for $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$

Atom	x	y	z	B(Å^2)
Ba(1)	0.84078(4)	−0.20817(3)	−0.04565(3)	1.296(4)
Se(1)	0.3047(1)	0.48634(7)	0.51191(6)	2.80(1)
Se(2)	0.3934(1)	0.18581(7)	0.53995(6)	2.43(1)
O(1)	0.5909(6)	−0.3330(5)	−0.1622(4)	2.11(7)
O(2)	0.2434(6)	−0.4772(4)	−0.1318(4)	1.78(6)
O(3)	0.1215(6)	−0.3483(5)	0.1623(4)	2.20(7)
O(4)	0.3975(6)	−0.1349(4)	0.1546(4)	1.91(7)
O(5)	0.2229(6)	−0.0520(5)	−0.1283(4)	2.14(7)
O(6)	0.9909(7)	−0.1347(6)	−0.3460(4)	3.07(9)

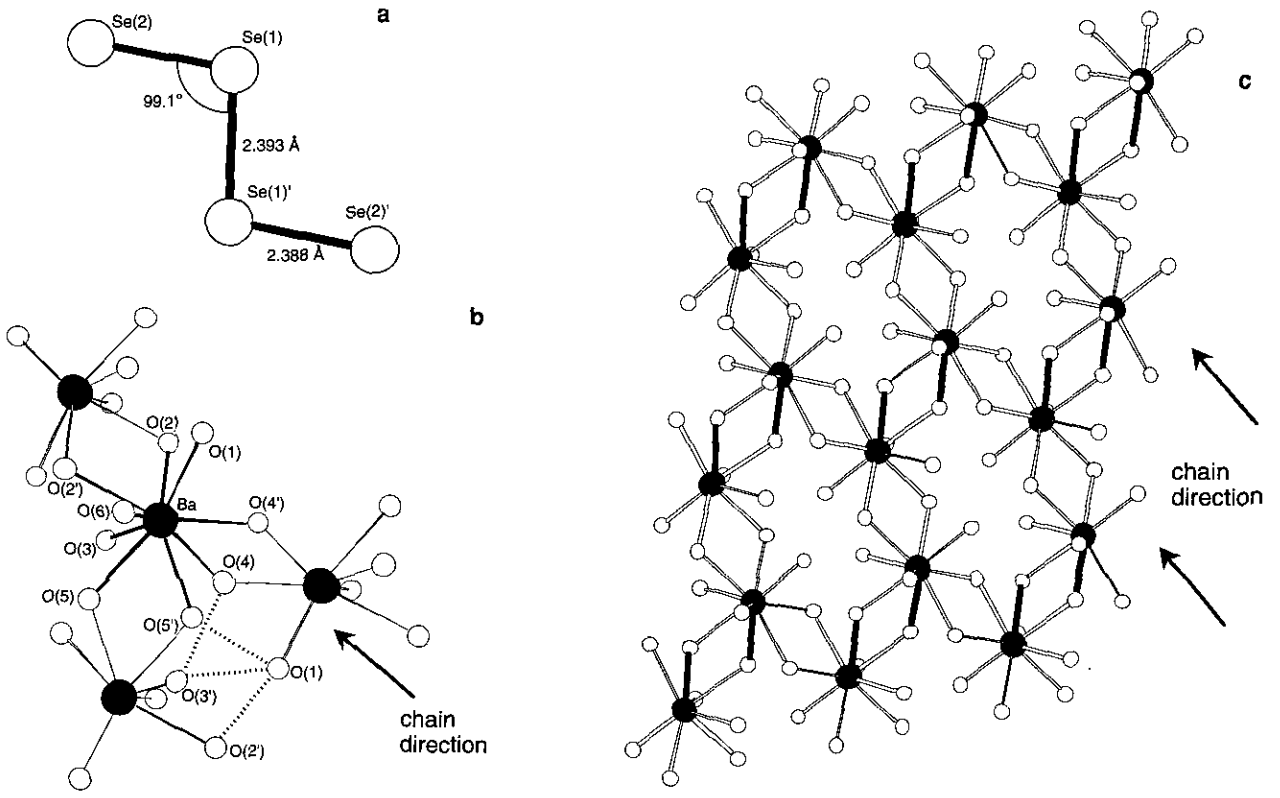

FIG. 2. (a) $[Se_4]^{2-}$ ion and (b) a view of the BaO_9 coordination geometry in the $^1_\infty[Ba(OH)(H_2O)_2(H_2O)_{6/2}]^+$ chains. The O ··· O interchain hydrogen bonding interactions are shown as dashed lines. (c) The $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ layers. The long interchain Ba–O(5′) interactions are in bold.

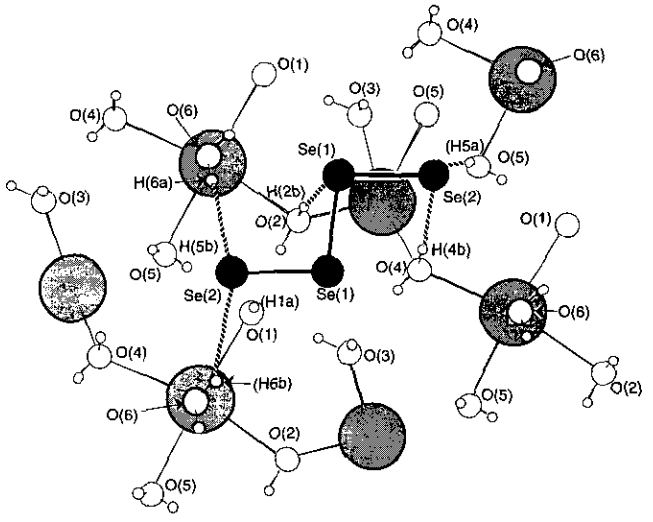

FIG. 3. Hydrogen bonding interactions (dashed lines) between the $[Se_4]^{2-}$ ions and the $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ layers. Only selected hydrogen atoms are shown for clarity.

fied through comparisons with the simulated XRD profile generated from parameters of the single crystal X-ray diffraction study.

X-Ray Structure Determination

A metallic gray block with crystal dimensions 0.22 × 0.28 × 0.41 mm was mounted on a glass fiber in a random orientation. Data collection was performed at 25°C with Mo$K\alpha$ radiation (λ = 0.71073 Å) on an Enraf–Nonius CAD4F computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Data were collected by using a $\theta/2\theta$ scan mode with a variable scan rate (0.67–8°/min). Periodic monitoring of three check reflections throughout data collection showed less than 1% decay.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections with $2\theta > 36°$. An empirical absorption correction (DIFABS) and Lorentz and polarization corrections were applied. Atomic scattering factors were taken from Cromer and Waber (14).

The data were indexed on a triclinic cell, space group $P\bar{1}$. The initial atomic coordinates for the three heavy

atoms were determined from a Patterson map and the remaining atoms located by successive least-squares refinements and difference Fourier syntheses. The hydrogen atoms were clearly visible in the final cycles of refinement. The structure was successfully refined (MolEN, Enraf–Nonius) using full-matrix least-squares with all atoms anisotropic (except the hydrogens) in the final cycles. The highest peak in the final difference map was 0.97 e/Å^3, which was located near Ba. The crystallographic data are summarized in Table 1. The final calculated and observed structure factors are available as supplementary material.[2]

RESULTS AND DISCUSSION

The $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ compound crystallizes in space group $P\bar{1}$ with alternating layers of $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ sheets and $[Se_4]^{2-}$ ions stacked normal to the (001) plane of the unit cell (Fig. 1). Listings of fractional coordinates and interatomic distances and angles for the $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ compound are given in Tables 2 and 3, respectively. The $[Se_4]^{2-}$ chains (Fig. 2a) are quite normal and isostructural with those in other $[Se_4]^{2-}$ salts (15–18). The Se(1)–Se(2) and Se(1)–Se(1′) contacts are 2.338(1) and 2.393(1) Å, respectively. Bonds to terminal chalcogenides are, in general, shorter than those on the interior of the polychalcogenide chains (17), and the $[Se_4]^{2-}$ ion is quite unremarkable in this regard.

The $[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ layer contains nine-coordinate Ba^{2+} ions with one terminal OH^- ligand (Ba–O(1) = 2.696(1) Å), two terminal H_2O ligands (Ba–O(3) = 2.825(1) Å, Ba–O(6) = 2.814(1) Å), and six bridging H_2O groups (Ba–O = 2.825(1)–2.949(1) Å) defining the distorted capped square antiprismatic coordination sphere. The Ba–O contacts to the water molecules are similar to those in other barium hydrate complexes, such as $BaCl_2 \cdot 2H_2O$ (19). The Ba–OH contact is longer than the reported Ba–O contacts to terminal alkoxides (e.g., $[H_3Ba_6O(O\text{-}t\text{-}Bu)_{11}(OCEtCH_2O)(THF)_3]$, Ba–O = 2.57 Å; however, the Ba^{2+} ions are only seven-coordinate in the alkoxide systems (20). The structure of $Ba(OH)_2$ is unknown (21).

The $^2_\infty[Ba_2(OH)_2(H_2O)_{10}]^{2+}$ network is best described as one-dimensional chains of formula $^1_\infty[Ba(OH)(H_2O)_2(H_2O)_{6/2}]^+$ containing nine-coordinate Ba^{2+} ions as shown in Fig. 2b. The chains are condensed into two-dimensional sheets (Fig. 2c) by virtue of long interchain Ba–O(5)–Ba contacts (Ba–O(5′) = 2.949(1) Å) that constitute the ninth coordination site of the Ba^{2+} ion. In addition, there are three interchain O–H · · · O hydrogen bonds to the hydroxyl oxygen (O · · · O = 2.65–2.68 Å) and one involving two water molecules on neighboring chains (O(4)–O(3′) = 2.77 Å) as illustrated in Fig. 2b. The relatively high negative charge on a hydroxyl oxygen makes it a good proton acceptor but the hydroxyl hydrogen is rarely involved in hydrogen bonding in the solid state (1).

Of particular interest are the seven O · · · Se interactions ranging from 3.44 to 3.63 Å listed in Table 4. Because of the high quality of the structural refinement, the hydrogen atoms were clearly visible in the later difference maps. Therefore, we can also examine the H · · · Se distances and O–H · · · Se angles in order to assess the nature and significance of the hydrogen bonding interactions. For a point of reference to sulfur, the sums of the O–S and S–H van der Waals (VDW) radii (2, 22) are 3.3 and 3.0 Å, respectively. Typical O–H · · · S hydrogen bonds display O–S contacts of 3.2–3.4 Å and H · · · S contacts of ~2.4

TABLE 3
Interatomic Contacts (Å) and Angles (°) for $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$

Atoms		Distance	Atoms		Distance
Ba(1)	O(1)	2.696(1)	Ba(1)	O(2)	2.825(1)
Ba(1)	O(2′)	2.864(1)	Ba(1)	O(3)	2.825(1)
Ba(1)	O(4)	2.842(1)	Ba(1)	O(4′)	2.842(1)
Ba(1)	O(5)	2.836(1)	Ba(1)	O(5′)	2.949(1)
Ba(1)	O(6)	2.814(1)	Se(1)	Se(1′)	2.393(1)
Se(1)	Se(2)	2.338(1)			

Atoms			Angle
O(1)	Ba(1)	O(2)	87.8(1)
O(1)	Ba(1)	O(3)	134.8(1)
O(1)	Ba(1)	O(4′)	90.2(1)
O(1)	Ba(1)	O(5′)	141.3(1)
O(2)	Ba(1)	O(2′)	73.3(1)
O(2)	Ba(1)	O(4)	143.5(1)
O(2)	Ba(1)	O(5)	76.3(1)
O(2)	Ba(1)	O(6)	71.8(1)
O(2′)	Ba(1)	O(4)	70.2(1)
O(2′)	Ba(1)	O(5)	135.3(1)
O(2′)	Ba(1)	O(6)	128.6(1)
O(3)	Ba(1)	O(4′)	133.1(1)
O(3)	Ba(1)	O(5′)	69.8(1)
O(4)	Ba(1)	O(4′)	75.5(1)
O(4)	Ba(1)	O(5′)	64.3(1)
O(4′)	Ba(1)	O(5)	79.8(1)
O(4′)	Ba(1)	O(6)	69.4(1)
O(5)	Ba(1)	O(6)	68.5(1)
Se(2)	Se(1)	Se(1′)	99.1(1)
Ba(1)	O(4)	Ba(1′)	104.5(1)

[2] See NAPS Document No. 05256 for 27 pages of supplementary materials. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Add $1.75 for postage of any microfiche orders.

TABLE 4
Potential Hydrogen Bonding Interactions for $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$

Atoms (O–H ··· X)	O ··· X (Å)	H ··· X (Å)	O–H ··· X (deg)
O(5), H(5*a*), Se(2)	3.44	2.61	165
O(4), H(4*b*), Se(2)	3.47	2.53	166
O(2), H(2*b*), Se(1)	3.51	2.52	169
O(6), (H6*a*,*b*), Se(1)	3.52	>3.1	
O(6), H(6*b*), Se(2)	3.58	2.89	146
O(1), H(1*a*), Se(2)	3.61	2.96	160
O(6), H(6*a*), Se(2)	3.63	2.79	172
O(2), H(2*a*), O(1)	2.65	1.79	171
O(3), H(3*b*), O(1)	2.67	1.80	178
O(5), H(5*b*), O(1)	2.68	2.02	170
O(4), H(4*a*), O(3)	2.77	2.00	166

Atoms			Angle
Se(1)	Se(1)	H(2*b*)	83
Se(2)	Se(1)	H(2*b*)	102
Se(1)	Se(2)	H(5*a*)	121
Se(1)	Se(2)	H(4*b*)	90
Se(1)	Se(2)	H(6*b*)	95
Se(1)	Se(2)	H(6*a*)	95

Å (23–26). For selenium, the sums of the VDW radii for O–Se and Se–H are 3.4 and 3.1 Å, respectively. Based on these data, one can assume that hydrogen bonding to selenium may be important if the O ··· Se contacts are ≤~3.5 Å and have hydrogen atoms that are properly oriented with H···Se contacts of ~2.5 Å. Most of the hydrogen bonding interactions reported by Krebs *et al.* (7–9) fall within these ranges. Three interactions in the $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ compound clearly fall within this range, namely, O(5)–H(5a)···Se(2), O(4)–H(4b)···Se(2), and O(2)–H(2b)···Se(1) as shown in Fig. 3. The last interaction is somewhat unexpected in that the negative charge of the Se_4^{2-} chain is primarily associated with the terminal Se(2) atoms, thus making them the most probable site of hydrogen bond formation. Although the O(6)···Se(2) contacts of 3.58 and 3.63 Å and the H(6a)···Se(2) and H(6b)···Se(2) contacts of 2.79 and 2.89 Å, respectively, are outside the expected range of strong hydrogen bonding interactions, the conspicuous extension of O(6) into the $[Se_4]^{2-}$ layer (see Fig. 1) and the relatively linear O(6)–H···Se(2) interactions (171° and 146°) suggest that some dipolar interactions do exist. The orientation of O(1)–H(1a) and Se(2) is suggestive of hydrogen bonding (Fig. 3), but the long H···Se separation of 2.96 Å and the fact that hydroxyl hydrogens are poor proton donors (1) suggest that these interactions are probably not significant.

In summary, the $[Ba_2(OH)_2(H_2O)_{10}][Se_4]$ compound displays an unusual hydrogen bonding network in the solid state with several O–H ··· Se hydrogen bonding interactions to an Se_4^{2-} chain. Although similar interactions have been observed with terminal *mono*selenides by Krebs *et al.*, hydrogen bonding to polyselenides was, to our knowledge, previously unknown.

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