

Diholmium(III) trisulfate tetrahydrate

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{S—O}) = 0.003$ Å; R factor = 0.047; wR factor = 0.130; data-to-parameter ratio = 12.4.

The single-crystal structure of the title compound [systematic name: poly[tetraaquatri- μ_2 -sulfato-diholmium(III)]], $[\text{Ho}_2(\text{SO}_4)_3(\text{H}_2\text{O})_4]_n$, features two-dimensional holmium(III) sulfate layers constructed by eight-coordinate holmium and sulfate groups. The coordination about Ho includes four O atoms from bridging sulfate ions. One S atom makes three S—O—Ho linkages through bridging O atoms, while a second S atom lies on a twofold axis and makes two S—O—Ho linkages. The coordination of each Ho atom is completed by four water molecules, which act as terminal ligands of Ho^{3+} .

Related literature

For related literature, see: Doran *et al.* (2002); Hummel *et al.* (1993); Li *et al.* (1998); Plévert *et al.* (2001); Xu, Fan, Chino *et al.* (2004); Xu, Fan, Elangovan *et al.* (2004); Xu, Ding, Feng *et al.* (2006); Xu, Ding, Zhou & Liu (2006); Yuan *et al.* (2004); Zhang *et al.* (2004); Xu *et al.* (2007).

Experimental

Crystal data

$[\text{Ho}_2(\text{SO}_4)_3(\text{H}_2\text{O})_4]$	$V = 1604.6$ (6) Å ³
$M_r = 762.17$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 13.466$ (3) Å	$\mu = 10.29$ mm ⁻¹
$b = 6.6966$ (15) Å	$T = 293$ (2) K
$c = 18.183$ (4) Å	$0.10 \times 0.08 \times 0.07$ mm
$\beta = 101.875$ (3)°	

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.426$, $T_{\max} = 0.533$
(expected range = 0.389–0.487)
4131 measured reflections

1725 independent reflections
1579 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.130$
 $S = 1.08$
1725 reflections
139 parameters

13 restraints
Only H-atom coordinates refined
 $\Delta\rho_{\text{max}} = 4.55$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.86$ e Å⁻³

Table 1

Selected bond lengths (Å).

Ho1—O6 ⁱ	2.287 (3)	Ho1—O5 ⁱⁱ	2.347 (3)
Ho1—O1	2.303 (3)	Ho1—O3	2.394 (3)
Ho1—O3W	2.308 (4)	Ho1—O2W	2.426 (4)
Ho1—O1W	2.344 (3)	Ho1—O4W	2.466 (3)

Symmetry codes: (i) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$; (ii) $-x + \frac{3}{2}, -y - \frac{1}{2}, -z + 1$.

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2059).

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supplementary materials

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Comment

Over the past decades, the synthesis of new two and three dimensional inorganic materials have received great attention, due to their functional applications. As the building elements of open-frameworks, not only silicon and germanium have been chosen to synthesize new frameworks (Li *et al.*, 1998; Plévert *et al.*, 2001; Xu *et al.*, 2004a; Xu *et al.*, 2004b), but also rare-earth elements. In the last few years, an important advance in solid inorganic materials has been achieved by study of lanthanide sulfates (Zhang *et al.*, 2004; Yuan *et al.*, 2004; Xu *et al.*, 2006a; Xu *et al.*, 2006b; Doran *et al.*, 2002, Xu *et al.*, 2007). In this work, we designed and synthesized the title compound, holmium(3+) sulfate octahydrate, which features a two-dimensional layered framework.

Similar to $\text{Eu}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$ (Xu *et al.*, 2007) and $\text{Gd}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$ (Hummel *et al.*, 1993), the layer of the title compound is constructed from HoO_8 polyhedra and SO_4 tetrahedra. The asymmetric unit contains 12 crystallographic independent non-hydrogen atoms, all of which belong to the inorganic framework. As show in Fig. 1, the coordination about Ho is achieved by four O atoms from bridging sulfate ions. S1 makes three S–O–Ho linkages through bridging O atoms, while S2 lies on a two fold axis and makes two S–O–Ho linkages. The coordination sphere of each Ho is completed by four water molecules, which act as terminal ligands of Ho^{3+} . To the best of our knowledge, although many lanthanide sulfates are known, this is the first example of holmium sulfate.

The bond distances and bond angles are in agreement with those found in the reported rare-earth compounds (Xu *et al.*, 2007). The geometry of the sulfate ions is unexceptional. Fig. 2 shows the two-dimensional arrangement in the unit cell, displaying the way the different Ho ions are connected by bridging sulfates and water molecules.

Experimental

Colorless block crystals were synthesized hydrothermally from a mixture of Ho_2O_3 , H_2SO_4 , H_2O and ethylenediamine. In a typical synthesis, Ho_2O_3 (0.2584 g) was dissolved in a mixture of 5 ml water, ethylenediamine (0.3651 g) and H_2SO_4 (98%) (0.2148 g) with constant stirring. Finally, the mixture was kept in a 25 ml Teflon-lined steel autoclave at 453 K for 6 days. The autoclave was slowly cooled to room temperature, and then the product was filtered, washed with distilled water, and dried at room temperature. Colorless block crystals of the title compound were obtained.

Refinement

The highest peak in the difference map is $4.55 \text{ e}/\text{\AA}^3$, and $0.94(2) \text{ \AA}$ from Ho_1 , while the minimum peak is $0.83(2) \text{ \AA}$ from Ho_1 . The H atom was located from a difference-Fourier map. Because the refinement for H atoms is not stable, the distances for H–O are restrained in the final refinement. All the H–O bond lengths are fixed as $0.85(2) \text{ \AA}$.

Figures

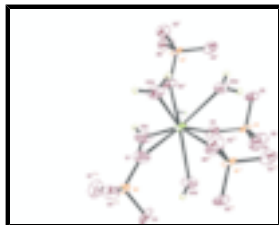


Fig. 1. The molecular structure for title compound. Displacement ellipsoids at the 70% probability level.

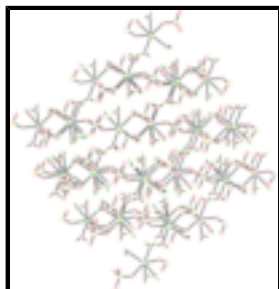


Fig. 2. The crystal packing in the unit cell of $\text{Ho}_2(\text{SO}_4)_3(\text{H}_2\text{O})_8$.

Poly[tetraaquatri- μ_2 -sulfato-diholmium(III)]

Crystal data

$[\text{Ho}_2(\text{SO}_4)_3(\text{H}_2\text{O})_4]$

$M_r = 762.17$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 13.466\ (3)\ \text{\AA}$

$b = 6.6966\ (15)\ \text{\AA}$

$c = 18.183\ (4)\ \text{\AA}$

$\beta = 101.875\ (3)^\circ$

$V = 1604.6\ (6)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1432$

$D_x = 3.155\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1579 reflections

$\theta = 2.8\text{--}27.0^\circ$

$\mu = 10.29\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Block, colorless

$0.10 \times 0.08 \times 0.07\ \text{mm}$

Data collection

Bruker APEX2 CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293\ (2)\ \text{K}$

ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 2003)

$T_{\min} = 0.426$, $T_{\max} = 0.533$

4131 measured reflections

1725 independent reflections

1579 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 27.0^\circ$

$\theta_{\min} = 2.3^\circ$

$h = -15 \rightarrow 17$

$k = -8 \rightarrow 8$

$l = -21 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.047$	Only H-atom coordinates refined
$wR(F^2) = 0.130$	$w = 1/[\sigma^2(F_o^2) + (0.0925P)^2]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
1725 reflections	$(\Delta/\sigma)_{\max} = 0.009$
139 parameters	$\Delta\rho_{\max} = 4.55 \text{ e } \text{\AA}^{-3}$
13 restraints	$\Delta\rho_{\min} = -2.86 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 1997a), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00497 (16)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ho1	0.833712 (14)	0.02050 (3)	0.607964 (10)	0.01160 (7)
S1	0.78096 (8)	-0.02655 (15)	0.41069 (6)	0.0116 (3)
S2	1.0000	0.3197 (2)	0.7500	0.0125 (3)
O1	0.9155 (2)	0.1928 (5)	0.71260 (17)	0.0239 (8)
O2	0.8377 (2)	-0.0344 (5)	0.3506 (2)	0.0219 (9)
O3	0.8517 (2)	-0.0730 (5)	0.48430 (16)	0.0153 (7)
O4	1.0348 (2)	0.4445 (5)	0.69329 (18)	0.0192 (8)
O5	0.6988 (2)	-0.1760 (5)	0.39806 (16)	0.0184 (8)
O6	0.7382 (2)	0.1712 (5)	0.41740 (17)	0.0211 (8)
O1W	0.9839 (2)	-0.1652 (5)	0.6397 (2)	0.0307 (10)
H1A	0.989 (3)	-0.2916 (17)	0.641 (3)	0.046*
H1B	1.0392 (12)	-0.101 (3)	0.646 (3)	0.046*
O2W	0.6576 (3)	-0.0171 (4)	0.5448 (2)	0.0199 (9)
H2A	0.6163 (18)	0.076 (3)	0.528 (3)	0.030*
H2B	0.6365 (12)	-0.106 (3)	0.5116 (12)	0.030*
O3W	0.7442 (3)	-0.0132 (5)	0.7027 (2)	0.0272 (11)

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H3A	0.6826 (11)	-0.045 (6)	0.6842 (17)	0.041*
H3B	0.7534 (16)	0.023 (5)	0.7492 (6)	0.041*
O4W	0.9593 (2)	0.2333 (5)	0.56423 (16)	0.0183 (8)
H4A	1.0001 (11)	0.172 (4)	0.5433 (12)	0.028*
H4B	0.992 (2)	0.309 (4)	0.5977 (15)	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ho1	0.00961 (13)	0.00923 (12)	0.01614 (14)	-0.00108 (5)	0.00306 (11)	-0.00041 (6)
S1	0.0102 (5)	0.0092 (5)	0.0160 (5)	-0.0012 (3)	0.0039 (4)	0.0008 (3)
S2	0.0096 (5)	0.0116 (7)	0.0159 (6)	0.000	0.0015 (5)	0.000
O1	0.0205 (14)	0.0269 (19)	0.0239 (16)	-0.0132 (14)	0.0032 (13)	-0.0038 (14)
O2	0.0153 (18)	0.0308 (18)	0.0211 (17)	-0.0025 (12)	0.0069 (15)	-0.0044 (13)
O3	0.0124 (12)	0.0193 (15)	0.0151 (13)	0.0017 (13)	0.0053 (11)	0.0023 (13)
O4	0.0172 (15)	0.0214 (16)	0.0212 (16)	-0.0008 (13)	0.0092 (13)	0.0067 (14)
O5	0.0136 (13)	0.0121 (15)	0.0287 (16)	-0.0049 (13)	0.0022 (12)	0.0002 (13)
O6	0.0250 (14)	0.0083 (14)	0.0299 (17)	0.0019 (13)	0.0052 (13)	0.0025 (13)
O1W	0.0127 (13)	0.0118 (16)	0.063 (2)	0.0014 (13)	-0.0016 (16)	0.0069 (17)
O2W	0.0170 (17)	0.0108 (15)	0.0287 (19)	0.0009 (11)	-0.0027 (17)	-0.0013 (12)
O3W	0.0206 (19)	0.045 (2)	0.0180 (19)	-0.0147 (13)	0.0087 (17)	-0.0067 (13)
O4W	0.0152 (13)	0.0208 (17)	0.0199 (15)	-0.0031 (13)	0.0058 (12)	-0.0043 (12)

Geometric parameters (\AA , $^\circ$)

Ho1—O6 ⁱ	2.287 (3)	S2—O1 ⁱⁱⁱ	1.470 (3)
Ho1—O1	2.303 (3)	S2—O4	1.477 (4)
Ho1—O3W	2.308 (4)	S2—O4 ⁱⁱⁱ	1.477 (4)
Ho1—O1W	2.344 (3)	O5—Ho1 ⁱⁱ	2.347 (3)
Ho1—O5 ⁱⁱ	2.347 (3)	O6—Ho1 ⁱ	2.287 (3)
Ho1—O3	2.394 (3)	O1W—H1A	0.849 (12)
Ho1—O2W	2.426 (4)	O1W—H1B	0.847 (14)
Ho1—O4W	2.466 (3)	O2W—H2A	0.849 (17)
S1—O2	1.457 (4)	O2W—H2B	0.855 (15)
S1—O6	1.459 (3)	O3W—H3A	0.855 (14)
S1—O5	1.474 (3)	O3W—H3B	0.866 (12)
S1—O3	1.507 (3)	O4W—H4A	0.839 (16)
S2—O1	1.470 (3)	O4W—H4B	0.845 (17)
O6 ⁱ —Ho1—O1	79.91 (11)	O2—S1—O6	111.8 (2)
O6 ⁱ —Ho1—O3W	88.51 (12)	O2—S1—O5	110.55 (19)
O1—Ho1—O3W	70.54 (12)	O6—S1—O5	109.45 (19)
O6 ⁱ —Ho1—O1W	146.85 (11)	O2—S1—O3	108.96 (19)
O1—Ho1—O1W	79.67 (12)	O6—S1—O3	107.54 (18)
O3W—Ho1—O1W	108.75 (13)	O5—S1—O3	108.37 (18)
O6 ⁱ —Ho1—O5 ⁱⁱ	144.18 (10)	O1—S2—O1 ⁱⁱⁱ	109.4 (3)
O1—Ho1—O5 ⁱⁱ	125.75 (11)	O1—S2—O4	109.32 (18)
O3W—Ho1—O5 ⁱⁱ	79.48 (11)	O1 ⁱⁱⁱ —S2—O4	108.85 (18)

O1W—Ho1—O5 ⁱⁱ	68.48 (10)	O1—S2—O4 ⁱⁱⁱ	108.85 (18)
O6 ⁱ —Ho1—O3	99.64 (11)	O1 ⁱⁱⁱ —S2—O4 ⁱⁱⁱ	109.32 (18)
O1—Ho1—O3	141.59 (11)	O4—S2—O4 ⁱⁱⁱ	111.0 (3)
O3W—Ho1—O3	147.65 (12)	S2—O1—Ho1	149.9 (2)
O1W—Ho1—O3	80.99 (12)	S1—O3—Ho1	127.75 (18)
O5 ⁱⁱ —Ho1—O3	75.70 (11)	S1—O5—Ho1 ⁱⁱ	143.27 (18)
O6 ⁱ —Ho1—O2W	70.48 (10)	S1—O6—Ho1 ⁱ	163.9 (2)
O1—Ho1—O2W	134.25 (12)	Ho1—O1W—H1A	127 (2)
O3W—Ho1—O2W	74.53 (14)	Ho1—O1W—H1B	117.0 (16)
O1W—Ho1—O2W	140.51 (11)	H1A—O1W—H1B	116 (3)
O5 ⁱⁱ —Ho1—O2W	73.80 (9)	Ho1—O2W—H2A	126.8 (19)
O3—Ho1—O2W	78.83 (12)	Ho1—O2W—H2B	123.8 (12)
O6 ⁱ —Ho1—O4W	72.75 (11)	H2A—O2W—H2B	99 (3)
O1—Ho1—O4W	74.56 (11)	Ho1—O3W—H3A	110 (2)
O3W—Ho1—O4W	142.73 (11)	Ho1—O3W—H3B	135.3 (16)
O1W—Ho1—O4W	76.79 (11)	H3A—O3W—H3B	113 (2)
O5 ⁱⁱ —Ho1—O4W	133.40 (11)	Ho1—O4W—H4A	114.7 (16)
O3—Ho1—O4W	68.87 (10)	Ho1—O4W—H4B	114 (2)
O2W—Ho1—O4W	125.16 (11)	H4A—O4W—H4B	109 (3)

Symmetry codes: (i) $-x+3/2, -y+1/2, -z+1$; (ii) $-x+3/2, -y-1/2, -z+1$; (iii) $-x+2, y, -z+3/2$.

Fig. 1

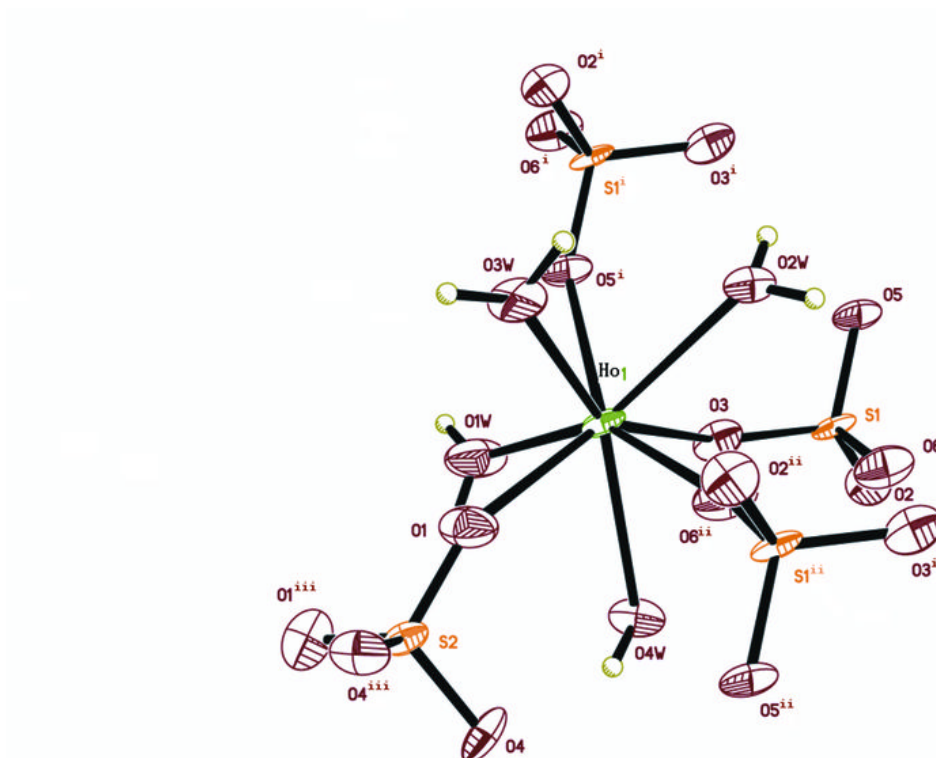


Fig. 2

