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Poly[[tetraaquadi-μ_5-fumarato-μ_4-fumarato-diholmium(III)] trihydrate]

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Key indicators

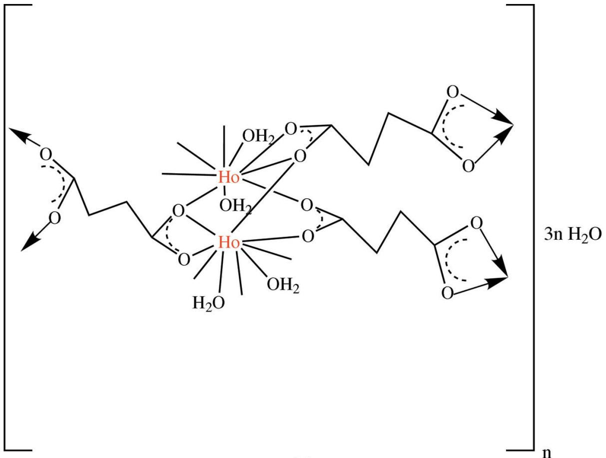
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.025
wR factor = 0.075
Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $\{[Ho_2(C_4H_2O_4)_3(H_2O)_4]\cdot 3H_2O\}_n$, is an open framework formed of corrugated layers built up from noncentrosymmetric binuclear units extended through $\mu_{1,3}$-bridges to give inorganic chains linked in the [100] direction. Additional connections in the [011] direction, through the ligands as spacers, give a three-dimensional structure exhibiting one-dimensional channels occupied by three solvent water molecules. The two independent water-coordinated Ho^{III} atoms each have a nine-coordination mode *via* seven O atoms from five carboxylate ligands in a tricapped trigonal prism and a monocapped square prism, respectively. Intralayer hydrogen bonds involve aqua ligands acting as donors, with carboxylate O atoms as acceptors.

Comment

By displaying some flexibility and multiple bond interactions, the fumarate anion can make the most of the well known modular nature of metal–organic frameworks and their resulting tunable properties. We have synthesized the title compound, (I), under hydrothermal conditions and have determined its structure. Compound (I) is the first holmium fumarate.



(I)

Compound (I) is isostructural with the europium and samarium analogues (Li & Zou, 2005; Zhang, Wang *et al.*, 2006; Zhang, Yang & Ma, 2006). Likewise, it is somewhat related to gadolinium fumarate (Manna *et al.*, 2006). Except for Pm and Tm, all other lanthanide fumarates have now been structurally studied (Michaelides *et al.*, 2003).

The asymmetric unit of (I) contains two Ho^{III} cations, three fumarate anions, and four coordinated and three uncoordi-

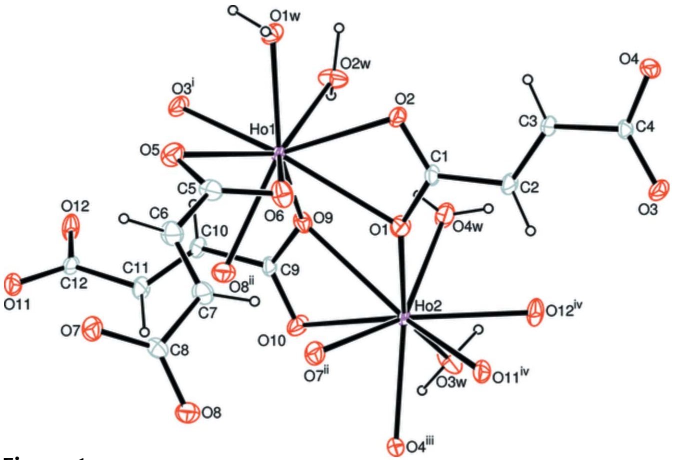


Figure 1
A segment of the polymeric structure of (I), showing the coordination environment, with 40% probability displacement ellipsoids (arbitrary spheres for H atoms). [Symmetry codes: (i) $-1 + x, y, z$; (ii) $1 - x, -y, -z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (iv) $1 + x, y, z$].

nated water molecules. Two $\mu_{1,1}$ oxo-bridges and one $\mu_{1,3}$ conventional carboxylate bridge link two Ho cations and form the basic building block (Fig. 1). Unlike the dimers recently reported for the Eu analogue (Li & Zou, 2005) or for the Ce coordination polymer formed with a saturated aliphatic dicarboxylate (Rahahlia *et al.*, 2006), this basic entity is not centrosymmetric. In the crystal structure of (I), the two independent metal atoms are nine-coordinate, each one surrounded by five fumarate ligands and two coordinated water molecules. Around Ho1, the coordination polyhedron is a slightly distorted tricapped trigonal prism, while Ho2 is at the centre of a monocapped square prism. The capping O atoms are, respectively, equatorial (O1*W*, O5, O8) and axial (O11) (Table 1).

The three independent fumarate anions have different coordination modes. Two (*L*1 and *L*2) are pentadentate in a *syn–anti* conformation, and they exhibit one $\mu_{1,1}$ bridge. However, *L*1 acts as bridging–chelating and bridging, exhibiting both $\mu_{1,1}$ and $\mu_{1,3}$ bridges, while *L*2 is bridging–chelating and bidentate. *L*3 is tetradentate, in a *syn–syn* conformation, and involves one function in a bidentate mode and the other in a $\mu_{1,3}$ bridge. With an Ho···Ho distance of 4.113 (2) Å, the one-edge-shared $Ho_2O_{12}(H_2O)_4$ bi-prisms are connected through $\mu_{1,3}$ bridges.

The structure of (I) can be described as a corrugated layer-type structure. The resulting three-dimensional framework exhibits one-dimensional channels parallel to [100] and occupied by three solvent water molecules (Fig. 2). Intralayer hydrogen bonds are observed, involving mainly aqua ligands acting as donors (O1*W*, O3*W*, O4*W*). Short hydrogen bonds are observed between coordinated water molecules and carboxylate O atoms (O4, O2, O10) (Table 2).

Experimental

A mixture of fumaric acid (0.176 g, 1.5 mmol), holmium(III) nitrate pentahydrate (0.441 g, 1.0 mmol) and sodium hydroxide (0.06 g, 1.5 mmol) in deionized water (15 ml) was introduced into a 23 ml Teflon-lined stainless steel vessel. The vessel was sealed and heated at 425 K for 1 d. After cooling to room temperature, single crystals of (I) were separated by filtration.

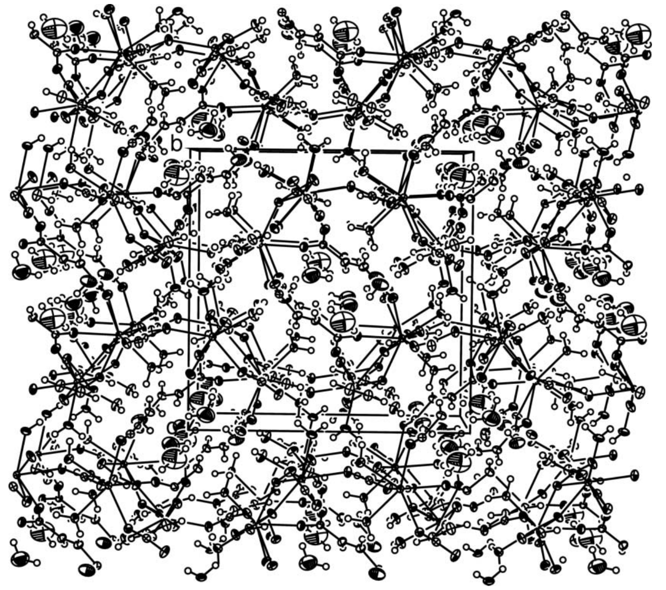


Figure 2
A packing diagram, viewed along the *a* axis.

Crystal data

$[Ho_2(C_4H_2O_4)_3(H_2O)_4]\cdot 3H_2O$
$M_r = 798.14$
Monoclinic, $P2_1/n$
$a = 9.4149$ (3) Å
$b = 14.6460$ (8) Å
$c = 14.6985$ (11) Å
$\beta = 91.005$ (5)°
$V = 2026.5$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 7.85$ mm^{-1}
$T = 298$ (2) K
0.56 × 0.30 × 0.18 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.054$, $T_{\max} = 0.188$
34506 measured reflections
5908 independent reflections
5381 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.090$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.075$
$S = 1.34$
5908 reflections
299 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.65$ e Å^{-3}
$\Delta\rho_{\min} = -2.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ho1—O3^{i}	2.313 (3)	Ho2—O7^{ii}	2.300 (3)
Ho1—O2*W*	2.362 (3)	Ho2—O3*W*	2.356 (3)
Ho1—O8^{ii}	2.396 (3)	Ho2—O1	2.367 (3)
Ho1—O1*W*	2.400 (3)	Ho2—O4*W*	2.379 (3)
Ho1—O9	2.416 (3)	Ho2—O4^{iii}	2.402 (3)
Ho1—O6	2.421 (3)	Ho2—O12^{iv}	2.423 (3)
Ho1—O2	2.436 (3)	Ho2—O10	2.441 (3)
Ho1—O5	2.502 (3)	Ho2—O11^{iv}	2.483 (3)
Ho1—O1	2.580 (3)	Ho2—O9	2.604 (3)
O10—Ho2—O1—Ho1	0.40 (17)	O3^{i}—Ho1—O5—C5	173.1 (3)
C12^{iv}—Ho2—O1—Ho1	−176.22 (15)		

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

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11···O12^{v}	0.96	1.96	2.912 (4)	171
O1*W*—H12···O4^{i}	0.96	1.75	2.681 (4)	163
O2*W*—H21···O11^{vi}	0.94	1.85	2.739 (4)	155
O2*W*—H22···O5*W*	0.95	1.89	2.820 (5)	166
O3*W*—H31···O2^{vii}	0.96	1.86	2.803 (4)	166
O3*W*—H32···O10^{viii}	0.96	1.81	2.756 (4)	169
O4*W*—H41···O5*W*	0.84	2.04	2.850 (5)	163
O4*W*—H42···O6^{vii}	0.83	1.98	2.809 (4)	171
O5*W*—H51···O6*W*^{ix}	0.81	1.99	2.77 (1)	159
O5*W*—H52···O5^{ix}	0.98	2.23	2.890 (5)	123
O6*W*—H61···O8^{ii}	0.97	2.09	2.935 (9)	146
O6*W*—H62···O7*W*^{ii}	0.86	2.08	2.831 (11)	146
O7*W*—H71···O11^{iv}	0.89	2.27	3.126 (7)	161
O7*W*—H72···O6*W*^{iv}	0.84	2.02	2.77 (1)	148
O7*W*—H72···O5*W*^{x}	0.84	2.42	2.954 (8)	122

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z$; (iv) $x+1, y, z$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (vii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (viii) $-x+1, -y+1, -z$; (ix) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (x) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

Methylene H atoms were placed in geometrically idealized positions, with C—H = 0.97 Å, and refined in riding mode, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Water H atoms were placed in chemically sensible positions based on hydrogen bonding and treated as riding, with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O). The highest electron density peak in the final difference Fourier map is 1.19 Å from Ho2 and the deepest hole is 0.70 Å from Ho1.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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