

Refinement

Refinement on F²R[F² > 2σ(F²)] = 0.032wR(F²) = 0.075

S = 1.024

1741 reflections

83 parameters

Only coordinates of H atom refined

$$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 1.12 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -1.43 \text{ e } \text{Å}^{-3}$$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)
Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

U _{iso} for H atom, U _{eq} = (1/3)Σ _i Σ _j U ^{ij} a _i [*] a _j [*] for all others.				
	x	y	z	U _{iso} /U _{eq}
Sr1	1/4	0.28088 (2)	1/4	0.00975 (11)
Sr2	0	0.11917 (3)	0.45274 (5)	0.00814 (10)
Fe1	1/4	0.46627 (4)	1/4	0.00809 (15)
Fe2	0	0.18264 (4)	0.06392 (8)	0.0078 (2)
F1	0.1994 (3)	0.39572 (11)	0.1356 (2)	0.0137 (5)
F2	0.2403 (3)	0.18836 (11)	0.0780 (2)	0.0144 (5)
F3	0.2919 (3)	0.03352 (11)	0.1268 (3)	0.0189 (5)
F4	0	0.3010 (2)	0.3880 (3)	0.0133 (7)
F5	0	0.1800 (2)	0.2468 (4)	0.0164 (7)
F6	0	0.4704 (2)	0.2890 (4)	0.0156 (7)
F7	0	0.28067 (15)	0.1019 (3)	0.0103 (6)
O1	0	0.0841 (2)	0.0472 (4)	0.0140 (8)
H1	0.098 (3)	0.0527 (19)	0.083 (4)	0.013

Table 2. Selected geometric parameters (Å, °)

Sr1—F4 × 2	2.494 (2)	Fe1—F1 × 2	1.908 (2)
Sr1—F7 × 2	2.529 (2)	Fe1—F3 ⁱⁱⁱ × 2	1.912 (2)
Sr1—F2 × 2	2.611 (2)	Fe1—F6 × 2	2.008 (1)
Sr1—F1 × 2	2.623 (2)	Fe2—F2 × 2	1.896 (3)
Sr1—F5 × 2	2.805 (3)	Fe2—F4 [*]	1.923 (4)
Sr2—F2 ⁱ × 2	2.480 (3)	Fe2—O1	1.965 (4)
Sr2—F3 ⁱ × 2	2.509 (2)	Fe2—F5	1.970 (4)
Sr2—F5	2.527 (4)	Fe2—F7	1.990 (3)
Sr2—F1 ⁱⁱ × 2	2.533 (3)	O1—H1	1.07 (3)
Sr2—F7 ⁱⁱⁱ	2.557 (3)		
Fe1 ^{vi} —F6—Fe1	155.4 (2)	H1 ^{vii} —O1—H1	92.8 (4)

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

The maximum residual electron density was found 1.0 Å from Sr1.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* option *PATT* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Bergerhoff, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1176). Services for accessing these data are described at the back of the journal.

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A Tricapped Trigonal Prismatic EuO(H₂O)₈ Site in Trihydrogen Tris(octaaquaeuropium) Dipotassium Digermanohexatitanooctadecatungstate(14−) Tridecahydrate

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Abstract

This paper reports the first observation of a tricapped trigonal prismatic EuO(H₂O)₈ site containing one anion O and eight aqua O atoms in K₂[Eu(H₂O)₈]₃H₃[(GeTi₃W₉O₃₇)₂O₃].13H₂O. Each half of the [(GeTi₃W₉O₃₇)₂O₃]^{14−} anion, which exhibits almost the same structure as the anion in K₉H₅[(GeTi₃W₉O₃₇)₂O₃].16H₂O, is coordinated by either three Eu³⁺ or two K⁺ atoms.

Comment

During the course of our studies of the crystal structures of photoluminescent polyoxometalloeuropates, the crystal fields of the Eu³⁺ sites in the polyoxotungstoeuropates and polyoxomolybdoeuropates have been characterized as a square antiprism and tricapped trigonal prism, respectively. Na₉[EuW₁₀O₃₆].32H₂O (Sugeta & Yamase, 1993) and K₁₅H₃[Eu₃(H₂O)₃(W₅O₁₈)₃(SbW₉O₃₃)].37H₂O (Yamase, Naruke & Sasaki, 1990) have square antiprismatic EuO₈ and EuO₆(H₂O)₂ sites, respectively. (NH₄)₁₂H₂[Eu₄(H₂O)₁₆(MoO₄)(Mo₇O₂₄)₄].13H₂O (Naruke, Ozeki & Yamase, 1991) and Eu₂(H₂O)₁₂(Mo₈O₂₇).6H₂O (Yamase & Naruke, 1991) have tricapped trigonal prismatic EuO₅(H₂O)₄ and EuO₃(H₂O)₆ sites, respectively. It has recently been found that Na₇H₁₉{[Eu₃O(OH)₃(OH₂)₃]₂Al₂(Nb₆O₁₉)₅} has bi-

capped trigonal prismatic $\text{EuO}_5(\text{OH})_2(\text{H}_2\text{O})$ sites where the Eu atoms are coordinated by both OH^- and H_2O groups (Ozeki, Yamase, Naruke & Sasaki, 1994). In all polyoxometalloeuropates, the photoexcitation of the $\text{O} \rightarrow \text{M}$ ligand-to-metal charge-transfer bands (LMCT) leads to the $f-f$ luminescence of Eu^{3+} as a result of the intramolecular energy transfer from the $\text{O} \rightarrow \text{M}$ LMCT states to 5D_1 and 5D_0 states of Eu^{3+} . Since the luminescence properties of the Eu^{3+} ion depend on the structural variety of the Eu^{3+} crystal fields, it has been proposed that the number of aqua ligands coordinated to the Eu^{3+} atom is an important factor in the deactivation of the 5D_0 state due to the weak vibronic coupling with vibrational states of the high-frequency OH oscillators of the aqua ligand (Yamase, 1994). This led us to expect that the plots of the reciprocal 5D_0 lifetimes against the known number of coordinated aqua ligands will produce a high correlation coefficient, as found for various aminopolycarboxylate Eu complexes (Horrocks & Sudnick, 1981). To obtain a meaningful plot for the polyoxometalloeuropates, further Eu^{3+} sites with a variety of aqua ligands should be structurally characterized. The present paper describes the crystal structure of $\text{K}_2[\text{Eu}(\text{H}_2\text{O})_8]_3\text{H}_3[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 1.13\text{H}_2\text{O}$, which exhibits the first tricapped trigonal prismatic $\text{EuO}(\text{H}_2\text{O})_8$ site containing one O anion and eight aqua ligands.

Fig. 1 shows the structure of $[\text{Eu}(\text{H}_2\text{O})_8]_3[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{5-}$. The framework of $[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{14-}$, which is isostructural with the anion in $\text{K}_9\text{H}_5[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 16\text{H}_2\text{O}$ (Yamase, Ozeki, Sakamoto, Nishiya & Yamamoto, 1993), is a condensed aggregate of two hypothetical $A-\alpha$ - $[\text{GeW}_9(\text{TiOH})_3\text{O}_{37}]^{7-}$ Keggin units that have lost three H_2O molecules by forming Ti—O—Ti bridges. The W—O [1.70(2)–2.31(2) Å] and Ti—O [1.82(2)–2.24(2) Å] bond distances in the $[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{14-}$ anion are almost the same as those in $\text{K}_9\text{H}_5[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 16\text{H}_2\text{O}$ [W—O 1.66(3)–2.38(2), Ti—O 1.78(2)–2.27(2) Å] (Yamase, Ozeki, Sakamoto, Nishiya & Yamamoto, 1993). The two central GeO_4 tetrahedra in the anion are nearly ideal, with Ge—O distances of 1.71(1)–1.75(2) Å and O—Ge—O angles of 108(1)–110.8(6)°, whereas the GeO_4 tetrahedra in $\text{K}_9\text{H}_5[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 16\text{H}_2\text{O}$ are slightly distorted with Ge—O distances ranging from 1.63(2) to 1.77(2) Å and O—Ge—O angles ranging from 107(1) to 113(1)°. One of the two half-anions of $[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{14-}$ coordinates to three Eu^{3+} cations and the other to two K^+ cations. The tricapped trigonal prismatic $\text{EuO}(\text{H}_2\text{O})_8$ site in the complex contains one terminal O atom (O6, O6' or O10) of the half-anion and eight aqua O atoms. One trigonal face of the Eu1 (Eu2) site is defined by O6 (O10) from the half-anion and

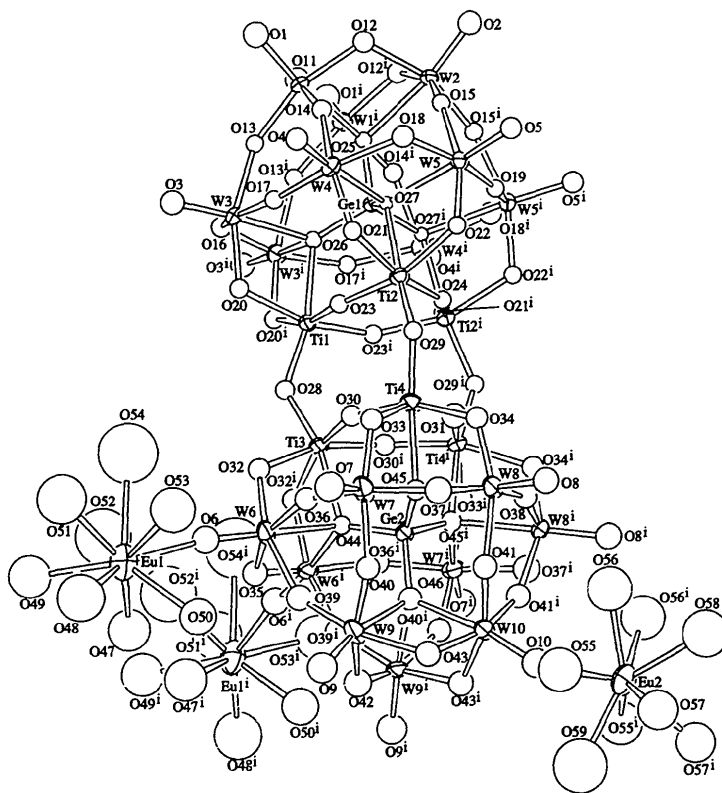


Fig. 1. ORTEP (Johnson, 1965) plot of the $[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{14-}$ anion and $[\text{Eu}(\text{H}_2\text{O})_8]_3$ units with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x, \frac{1}{2} - y, z$]

two aqua O atoms O47 and O52 (O56 and O56ⁱ) and the other trigonal face by three aqua O atoms O48, O51 and O53 (O57, O57ⁱ and O59). The three approximately rectangular faces are then capped by the aqua O atoms O49, O50 and O54 (O55, O55ⁱ and O58). The crystallographic site symmetries of the Eu1 and Eu2 sites are C_1 and C_s , respectively. The Eu—O bond lengths [2.42 (3)–2.45 (5) Å] for the prism vertices of both the Eu1 and Eu2 sites are similar. These distances are comparable to the bond distance [2.415 (1) Å] for the vertices of the tricapped trigonal prismatic $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$ site in $\text{Eu}(\text{H}_2\text{O})_9(\text{C}_2\text{H}_5\text{SO}_4)_3$ (Gerkin & Reppart, 1984). For the three capping O atoms at both the Eu1 and Eu2 sites, the Eu1—O54 distance [2.88 (5) Å] is extremely long compared with other Eu—O distances [Eu1—O49 2.46 (3), Eu1—O50 2.48 (3), Eu2—O55 or —O55ⁱ 2.59 (3), Eu2—O58 2.40 (5) Å]. The capping O

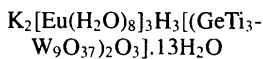
atom for the Eu site in $\text{Eu}(\text{H}_2\text{O})_9(\text{C}_2\text{H}_5\text{SO}_4)_3$ has an Eu—O bond distance of 2.542 Å (Gerkin & Reppart, 1984). There is no significant difference in the distance from the capping O atom to its least-square face among atoms O49, O50 and O54 (1.63, 1.86 and 1.77 Å, respectively). However, it should be noted that the distance from Eu1 to the least-square face is asymmetric: the O54-facing plane and Eu1 are 1.08 Å apart, while the O49- and O50-facing planes are 0.77 and 0.58 Å apart, respectively. Such a displacement of Eu1 from the center of the trigonal prism toward the O47···O48 edge is due to short O6···O53 and O51···O52 distances (2.94 and 3.48 Å, respectively) compared with the O47···O48 distance (3.97 Å), with a resultant elongation of the Eu1—O54 distance.

There are eight O atoms surrounding the K^+ cation with $\text{K}^+ \cdots \text{O}$ distances less than 3.3 Å: one is the lattice water O66 atom having a $\text{K}^+ \cdots \text{O}$ distance of 2.96 (5) Å, four belong to the half-anion with distances of 2.96 (2)–3.08 (2) Å, and three belong to the neighboring half-anion with distances of 3.00 (2)–3.29 (2) Å (Fig. 2). The observation of three Eu^{3+} and two K^+ cations per $[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3]^{14-}$ anion indicates that the complex can be formulated as $\text{K}_2[\text{Eu}(\text{H}_2\text{O})_8]_3\text{H}_3[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 1.13\text{H}_2\text{O}$ for its charge neutrality. As was anticipated, the lifetime of the 5D_0 luminescence of the title compound (~ 0.14 ms at 30 K) is the shortest among known polyoxometal-luorates. $\text{Eu}_2(\text{H}_2\text{O})_{12}(\text{Mo}_8\text{O}_{27}) \cdot 6\text{H}_2\text{O}$, in which the $\text{Eu}_3(\text{H}_2\text{O})_6$ site contains six aqua ligands coordinating to Eu^{3+} , has the next shortest lifetime (0.17 ms at 300 K) of the 5D_0 luminescence.

Experimental

$\text{K}_9\text{H}_5[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 1.16\text{H}_2\text{O}$ was prepared according to Yamase, Ozeki, Sakamoto, Nishiya & Yamamoto (1993). 0.5 g of $\text{K}_9\text{H}_5[(\text{GeTi}_3\text{W}_9\text{O}_{37})_2\text{O}_3] \cdot 1.16\text{H}_2\text{O}$ was dissolved in 10 ml water and aqueous KOH was added dropwise to adjust the pH to 5.8. 1 ml of an aqueous solution containing 0.07 g $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was added dropwise to the above solution at room temperature. The pH of the solution was adjusted to 2.8 with diluted HNO_3 solution. Colorless crystals were isolated from the solution after 3 d.

Crystal data



$M_r = 6177.5$

Monoclinic

$P2_1/m$

$a = 13.177$ (2) Å

$b = 18.645$ (3) Å

$c = 21.800$ (3) Å

$\beta = 99.82$ (1)°

$V = 5277$ (1) Å³

$Z = 2$

$D_x = 3.89$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 25 reflections

$\theta = 10.0$ – 12.5°

$\mu = 22.5$ mm⁻¹

$T = 296$ K

Needle

$0.5 \times 0.2 \times 0.2$ mm

Colorless

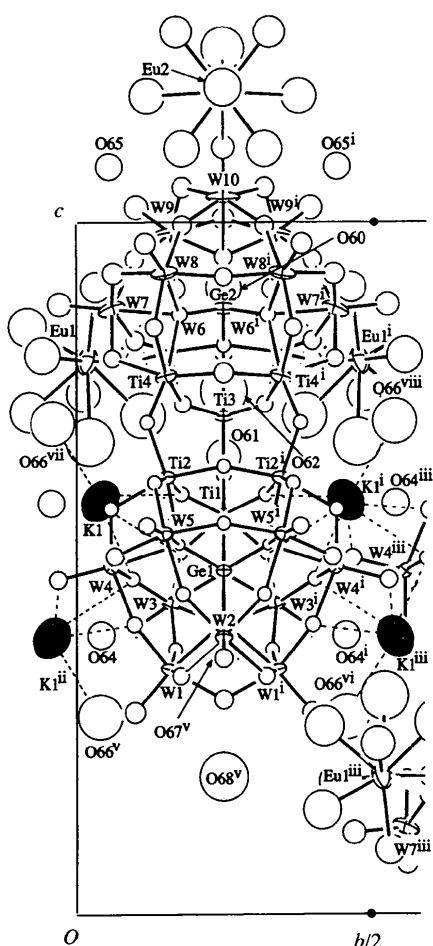


Fig. 2. Part of the unit cell viewed along the a axis. K atoms are represented by the shaded ellipsoids. The broken lines represent $\text{K}^+ \cdots \text{O}$ bonds less than 3.3 Å. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $-x, -y, 1 - z$; (iii) $-x, \frac{1}{2} + y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $x, y, -1 + z$; (vi) $x, \frac{1}{2} - y, -1 + z$; (vii) $-x, -y, 2 - z$; (viii) $-x, \frac{1}{2} + y, 2 - z$; (ix) $-x, 1 - y, 2 - z$.]

Data collection

AFC-5R diffractometer
 ω -2 θ scans
 Absorption correction:
 empirical via ψ scan
 (North, Phillips &
 Mathews, 1968)
 $T_{\min} = 0.004$, $T_{\max} = 0.011$
 13 015 measured reflections
 12 491 independent
 reflections

7874 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\max} = 27.5^\circ$
 $h = 0 \rightarrow 17$
 $k = 0 \rightarrow 24$
 $l = -28 \rightarrow 27$
 3 standard reflections
 every 150 reflections
 intensity decay: 0.80%

Refinement

Refinement on F
 $R = 0.066$
 $wR = 0.057$
 $S = 2.300$
 7874 reflections
 401 parameters
 H atoms not located
 $w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.07$
 $\Delta\rho_{\max} = 4.12 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -4.89 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

O24	-0.213 (2)	1/4	0.649 (1)	0.020 (5)
O25	-0.294 (2)	1/4	0.422 (1)	0.017 (5)
O26	-0.095 (2)	1/4	0.495 (1)	0.017 (5)
O27	-0.256 (1)	0.1748 (8)	0.5354 (6)	0.012 (3)
O28	0.135 (2)	1/4	0.637 (1)	0.024 (6)
O29	-0.143 (1)	0.1198 (9)	0.7128 (7)	0.021 (4)
O30	0.062 (1)	0.1804 (9)	0.7393 (7)	0.029 (4)
O31	-0.085 (2)	1/4	0.784 (1)	0.041 (7)
O32	0.266 (1)	0.1767 (9)	0.7339 (7)	0.030 (4)
O33	0.025 (1)	0.061 (1)	0.8041 (8)	0.031 (4)
O34	-0.127 (1)	0.1317 (9)	0.8481 (7)	0.030 (4)
O35	0.407 (2)	1/4	0.815 (1)	0.041 (7)
O36	0.225 (1)	0.100 (1)	0.8297 (8)	0.035 (5)
O37	0.015 (1)	0.063 (1)	0.9268 (9)	0.047 (5)
O38	-0.090 (2)	1/4	0.922 (1)	0.033 (6)
O39	0.365 (1)	0.167 (1)	0.9047 (8)	0.043 (5)
O40	0.219 (1)	0.099 (1)	0.9471 (8)	0.036 (5)
O41	0.051 (1)	0.180 (1)	0.9963 (8)	0.037 (5)
O42	0.393 (2)	1/4	1.006 (1)	0.050 (8)
O43	0.246 (1)	0.180 (1)	1.0514 (8)	0.040 (5)
O44	0.220 (2)	1/4	0.824 (1)	0.022 (5)
O45	0.058 (1)	0.1749 (9)	0.8669 (7)	0.026 (4)
O46	0.209 (2)	1/4	0.951 (1)	0.034 (7)
O47	0.656 (2)	0.131 (2)	0.836 (1)	0.12 (1)
O48	0.668 (3)	-0.083 (2)	0.850 (2)	0.15 (1)
O49	0.725 (2)	0.012 (2)	0.754 (1)	0.12 (1)
O50	0.528 (2)	0.033 (2)	0.907 (1)	0.090 (9)
O51	0.573 (3)	-0.079 (2)	0.728 (2)	0.16 (1)
O52	0.576 (3)	0.113 (3)	0.723 (2)	0.21 (2)
O53	0.423 (3)	-0.058 (2)	0.809 (2)	0.13 (1)
O54	0.427 (4)	0.023 (3)	0.685 (2)	0.24 (2)
O55	0.063 (2)	0.121 (2)	1.184 (1)	0.13 (1)
O56	-0.107 (2)	0.180 (2)	1.107 (1)	0.13 (1)
O57	-0.028 (2)	0.171 (2)	1.276 (1)	0.11 (1)
O58	-0.187 (4)	1/4	1.196 (2)	0.15 (2)
O59	0.165 (5)	1/4	1.252 (3)	0.19 (2)
O60	0.598 (4)	1/4	0.907 (2)	0.13 (2)
O61	0.420 (3)	1/4	0.664 (2)	0.12 (2)
O62	0.667 (5)	1/4	0.758 (3)	0.23 (2)
O63	0.269 (1)	0.152 (1)	0.5887 (9)	0.052 (6)
O64	-0.533 (2)	0.042 (1)	0.403 (1)	0.076 (8)
O65	0.112 (2)	0.057 (1)	1.082 (1)	0.074 (8)
O66	-0.038 (3)	0.041 (3)	1.286 (2)	0.20 (2)
O67	0.211 (3)	1/4	1.374 (2)	0.09 (1)
O68	0.345 (6)	1/4	1.198 (3)	0.25 (2)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

U_{iso} for O atoms, $U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$ for all others.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
W1	-0.27698 (7)	0.15945 (7)	0.35247 (4)	0.0259 (3)
W2	-0.4701 (1)	1/4	0.40005 (6)	0.0228 (4)
W3	-0.01370 (7)	0.15968 (7)	0.44902 (4)	0.0242 (3)
W4	-0.22973 (8)	0.05854 (6)	0.50312 (5)	0.0251 (3)
W5	-0.42066 (7)	0.14950 (6)	0.55094 (4)	0.0222 (3)
W6	0.33321 (8)	0.16071 (9)	0.81384 (5)	0.0429 (4)
W7	0.12446 (9)	0.05984 (8)	0.87476 (6)	0.0432 (4)
W8	-0.06228 (8)	0.14950 (8)	0.92783 (5)	0.0385 (4)
W9	0.32466 (9)	0.1599 (1)	0.98421 (5)	0.0572 (4)
W10	0.1374 (1)	1/4	1.03778 (7)	0.0521 (6)
Eu1	0.5683 (1)	0.0190 (1)	0.80097 (9)	0.0580 (6)
Eu2	-0.0071 (2)	1/4	1.1896 (1)	0.072 (1)
Ge1	-0.2256 (3)	1/4	0.4970 (2)	0.019 (1)
Ge2	0.1356 (3)	1/4	0.8763 (2)	0.034 (1)
Ti1	0.0174 (5)	1/4	0.5797 (3)	0.023 (1)
Ti2	-0.1860 (3)	0.1524 (3)	0.6328 (2)	0.024 (1)
Ti3	0.1541 (5)	1/4	0.7218 (3)	0.028 (1)
Ti4	-0.0461 (3)	0.1522 (3)	0.7781 (2)	0.03 (1)
K1	0.050 (1)	0.0418 (7)	0.5999 (6)	0.142 (6)
O1	-0.279 (1)	0.100 (1)	0.2912 (9)	0.042 (5)
O2	-0.598 (2)	1/4	0.370 (1)	0.036 (7)
O3	0.055 (1)	0.101 (1)	0.4140 (8)	0.038 (5)
O4	-0.221 (1)	-0.031 (1)	0.4840 (8)	0.032 (4)
O5	-0.540 (1)	0.119 (1)	0.5628 (7)	0.029 (4)
O6	0.427 (2)	0.102 (1)	0.8017 (9)	0.049 (6)
O7	0.164 (2)	-0.029 (1)	0.8823 (9)	0.056 (6)
O8	-0.153 (1)	0.117 (1)	0.9702 (9)	0.043 (5)
O9	0.414 (2)	0.102 (1)	1.023 (1)	0.059 (6)
O10	0.102 (2)	1/4	1.110 (1)	0.054 (9)
O11	-0.271 (2)	1/4	0.310 (1)	0.038 (7)
O12	-0.423 (1)	0.1770 (9)	0.3438 (7)	0.029 (4)
O13	-0.135 (1)	0.1675 (9)	0.3820 (7)	0.020 (4)
O14	-0.283 (1)	0.0983 (9)	0.4186 (7)	0.025 (4)
O15	-0.462 (1)	0.1807 (9)	0.4629 (7)	0.021 (4)
O16	0.026 (2)	1/4	0.417 (1)	0.026 (6)
O17	-0.100 (1)	0.0954 (9)	0.4847 (7)	0.021 (4)
O18	-0.374 (1)	0.065 (1)	0.5179 (8)	0.032 (4)
O19	-0.429 (2)	1/4	0.567 (1)	0.020 (5)
O20	0.069 (1)	0.1763 (9)	0.5237 (7)	0.023 (4)
O21	-0.182 (1)	0.0581 (9)	0.5876 (7)	0.022 (4)
O22	-0.338 (1)	0.1322 (8)	0.6257 (7)	0.020 (4)
O23	-0.061 (1)	0.1786 (9)	0.6094 (7)	0.021 (4)

Table 2. Selected bond lengths (\AA)

Eu1—O6	2.43 (2)	Eu2—O57	2.45 (3)
Eu1—O47	2.44 (3)	Eu2—O58	2.40 (5)
Eu1—O48	2.44 (4)	Eu2—O59	2.44 (6)
Eu1—O49	2.46 (3)	K1—O3'	3.00 (2)
Eu1—O50	2.48 (3)	K1—O4'	3.14 (2)
Eu1—O51	2.43 (4)	K1—O17	3.08 (2)
Eu1—O52	2.45 (5)	K1—O17'	3.29 (2)
Eu1—O53	2.42 (3)	K1—O20	3.04 (2)
Eu1—O54	2.88 (5)	K1—O21	3.03 (2)
Eu2—O10	2.44 (3)	K1—O23	2.96 (2)
Eu2—O55	2.59 (3)	K1—O66''	2.96 (5)
Eu2—O56	2.42 (3)		

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

As shown in Fig. 2, the ellipsoids for Ti3, Ti4, W6–W10 and Ge2 in the half-anion coordinating to the three Eu atoms are elongated in the direction approximately perpendicular to the mirror plane. In addition, average U_{eq} or U_{iso} values for Ti, W, Ge and O atoms in this half-anion (0.029, 0.046, 0.034 and 0.039 \AA^2 , respectively) are considerably larger than those for the corresponding atoms in the other half-anion (0.024, 0.024, 0.019 and 0.026 \AA^2 , respectively). These observations indicate that the crystal contains a distorted $[\text{Eu}(\text{H}_2\text{O})_8]_3[\text{GeTi}_3\text{W}_9\text{O}_{37}]_2\text{O}_3]^{5-}$ anion in which the half-anion coordinated to the three Eu atoms shifts slightly from its idealized position toward either side of the mirror plane.

Such a distortion of the anion would be induced by a slight shift of the Eu1 (and Eu1¹) position, which is associated with the displacement of several aqua ligands, especially atoms O52 and O54, which have large U_{iso} values of 0.21 (2) and 0.24 (2) Å², respectively. The coordination of a large number (eight) of aqua ligands and one O atom from the half-anion to an Eu atom explains the shift of the Eu atom due to the disordered structure of aqua ligands, which leads to the displacement of W, Ti and Ge atoms in the half-anion. The rather large residual maximum and minimum Fourier peaks (4.12 and -4.89 e Å⁻³, respectively) are located around the W9 atom at short distances of 0.48 and 1.05 Å, respectively. This is due to the large displacement of the W9 atom compared with the other atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *SIR88* (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1005). Services for accessing these data are described at the back of the journal.

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A Caesium Zinc Phosphate Constructed from Ladder-Like Four-Ring Chains

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Abstract

The synthesis, thermal properties and crystal structure of caesium trizinc bis[hydrogenphosphate(2-)] phosphate, Cs[Zn₃(HPO₄)₂(PO₄)], are described. This new caesium zinc phosphate has a three-dimensional framework structure containing one-dimensional channels.

Comment

Divalent metal phosphates are of interest for a number of reasons, one of which is that they can form framework structures which are zeolite-like (Gier & Stucky, 1991). Zeolites are aluminosilicates containing cages and channels, and can be used for a variety of commercial applications such as heterogeneous catalysis, ion exchange and adsorption (Breck, 1974). In our search for novel framework structures based on divalent metal phosphates and arsenates (Feng, Bu & Stucky, 1995, 1997a,b; Bu, Feng & Stucky, 1996; Bu, Gier & Stucky, 1996; Feng, Bu, Tolbert & Stucky, 1997), we discovered a new caesium zinc phosphate. The synthesis, crystal structure and thermal properties of this material are reported here.

The asymmetric unit is Cs[Zn₃(HPO₄)₂(PO₄)]. All three unique Zn sites have tetrahedral coordination geometry. Of the 12 O atoms, two (O11 and O12) are terminating hydroxyl groups on P2 and P3, and two (O2 and O3) are trigonally coordinated (excluding the possible coordination to the extra framework Cs atoms) between two Zn cations and one P cation. The other eight O atoms are bicoordinated between one Zn cation and one P cation. The presence of trigonally coordinated O atoms and the associated three-membered rings (six-membered rings if O atoms are included) involving two Zn atoms and one P atom usually leads to a dense framework and is a feature that distinguishes this salt from zeolite-like open-framework zincophosphates.

The framework contains channels along the crystallographic *a* axis (Fig. 1). The rectangularly shaped window of each channel is elongated along the unit-cell *c* axis and the frame of the window opening contains as many as 16 tetrahedral atoms. The three-dimensional framework of this compound comprises structural units which are commonly used to build zeolite structures: