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Redetermination of $[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Eu}-\text{O}) = 0.002$ Å; R factor = 0.015; wR factor = 0.032; data-to-parameter ratio = 26.7.

The crystal structure of the title compound, hexaaquachloridoeuropium(III) chloride, was redetermined with modern crystallographic methods. In comparison with the previous study [Lepert *et al.* (1983). *Aust. J. Chem.* **36**, 477–482], it could be shown that the atomic coordinates of some O atoms had been confused and now were corrected. Moreover, it was possible to freely refine the positions of the H atoms and thus to improve the accuracy of the crystal structure. $[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$ crystallizes with the $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ structure-type, exhibiting discrete $[\text{EuCl}_2(\text{H}_2\text{O})_6]^+$ cations as the main building blocks. The main blocks are linked with isolated chloride anions *via* $\text{O}-\text{H} \cdots \text{Cl}$ hydrogen bonds into a three-dimensional framework. The Eu^{3+} cation is located on a twofold rotation axis and is coordinated in the form of a Cl_2O_6 square antiprism. One chloride anion coordinates directly to Eu^{3+} , whereas the other chloride anion, situated on a twofold rotation axis, is hydrogen bonded to six octahedrally arranged water molecules.

Related literature

For previous structure determinations of the title compound, see: Lepert *et al.* (1983); Bel'skii & Struchkov (1965). For the $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ structure type and isotypic compounds, see: Marezio *et al.* (1961); Bell & Smith (1990); Burns & Peterson (1971); Graeber *et al.* (1966); Habenschuss & Spedding (1980); Hoch & Simon (2008); Junk *et al.* (1999); Reuter *et al.* (1994). For related structures, see: Demyanets *et al.* (1974); Reuter *et al.* (1994). For standardization of crystal data, see: Gelato & Parthé (1987).

Experimental

Crystal data

$[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$ $c = 7.929$ (3) Å
 $M_r = 366.41$ $\beta = 93.653$ (13)°
 Monoclinic, $P2_1/n$ $V = 498.4$ (2) Å³
 $a = 9.6438$ (12) Å $Z = 2$
 $b = 6.5322$ (10) Å Ag $K\alpha$ radiation

$\lambda = 0.56083$ Å
 $\mu = 3.74$ mm⁻¹

$T = 293$ K
 $0.23 \times 0.20 \times 0.18$ mm

Data collection

Stoe IPDS I diffractometer
 Absorption correction: multi-scan
 (*MulScanAbs* in *PLATON*;
 Spek, 2009)
 $T_{\min} = 0.425$, $T_{\max} = 0.510$

13401 measured reflections
 1762 independent reflections
 1653 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.043$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.015$
 $wR(F^2) = 0.032$
 $S = 1.03$
 1762 reflections

66 parameters
 All H-atom parameters refined
 $\Delta\rho_{\text{max}} = 0.63$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.77$ e Å⁻³

Table 1

Selected bond lengths (Å).

Eu1—O1	2.4618 (15)	Eu1—O3	2.3078 (16)
Eu1—O2 ⁱ	2.4620 (18)	Eu1—Cl1 ⁱⁱ	2.7690 (12)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O1—H1 ⁱ ···Cl2 ^j	0.74 (4)	2.36 (4)	3.081 (2)	166.08
O2—H2 ⁱ ···Cl1 ⁱⁱⁱ	0.81 (3)	2.54 (3)	3.351 (2)	174.97
O2—H3 ⁱ ···Cl2 ^{iv}	0.76 (4)	2.51 (4)	3.2234 (19)	157.37
O3—H4 ⁱ ···Cl1 ⁱ	0.72 (4)	2.35 (4)	3.036 (2)	160.44
O1—H5 ⁱ ···Cl1	0.74 (2)	2.36 (3)	3.095 (2)	173.89
O3—H6 ⁱ ···Cl2 ^{vi}	0.79 (4)	2.53 (4)	3.310 (2)	170.66

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

Data collection: *X-AREA* (Stoe & Cie, 2006); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2007); software used to prepare material for publication: *SHELXL97*.

Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5012).

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supporting information

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Redetermination of $[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$

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S1. Comment

$[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$ crystallizes with the $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ structure type (Marezio *et al.*, 1961), like many metal trichloride hexahydrates $M\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ with $M = \text{Y}$ (Bell & Smith, 1990), Ce (Reuter *et al.*, 1994), Nd (Habenschuss & Spedding, 1980), Sm - Tm (Graeber *et al.*, 1966), Am, Bk (Burns & Peterson, 1971), and three bromide hexahydrates $M\text{Br}_3 \cdot 6\text{H}_2\text{O}$ with $M = \text{Pr}$, Dy (Junk *et al.*, 1999) and Eu (Hoch & Simon, 2008). The first structure determination of the title compound was performed on the basis of film data (Bel'skii & Struchkov, 1965) and without determination of the hydrogen atom positions. A first exact structure determination with all atomic positions was performed by Lepert *et al.* (1983). However, the published data contain errors in the atomic coordinates. We have thus redetermined the structure on the basis of modern area detector data.

The Eu^{3+} cation in $[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$ is located on a twofold rotation axis and is coordinated in form of a distorted square antiprism defined by six water molecules and two chloride anions (Fig. 1, Table 1). Hydrogen bonds $\text{O}—\text{H}\cdots\text{Cl}$ connect the $[\text{EuCl}_2(\text{H}_2\text{O})_6]^+$ cations with the Cl^- counter-anions to a three-dimensional framework (Fig 2). The complexing chloride anion Cl1 is surrounded by three, the isolated chloride anion Cl2 by six H atoms (Figs. 3, 4), forming hydrogen bonds with $\text{Cl}\cdots\text{H}$ distances between 2.36 (4) and 2.54 (3) Å (Table 2) and are in good agreement with those in other chloride hydrates. The $\text{Eu}^{\text{III}}—\text{O}$ distances in $[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$ range from 2.3078 (16) to 2.4620 (18) Å and are comparable with those in $\text{EuCl}_3 \cdot 3\text{H}_2\text{O}$ (2.39–2.40 Å; Reuter *et al.*, 1994), $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (2.39–2.43 Å; Graeber *et al.*, 1966), or $\text{EuCl}(\text{OH})_2$ (2.35–2.44 Å; Demyanets *et al.*, 1974) and also with those in $\text{EuBr}_3 \cdot 6\text{H}_2\text{O}$ (Hoch & Simon, 2008).

S2. Experimental

The title compound was obtained by adding small portions of commercially available Eu_2O_3 (Alfa Aesar, 99.99%) into concentrated aqueous HCl solution at 353 K until only minor amounts of undissolved Eu_2O_3 remained visible for several minutes. The surplus Eu_2O_3 finally was dissolved by dropwise addition of concentrated HCl to the solution until a clear colourless solution was obtained. The solution was allowed to cool to 293 K, yielding colourless single-crystal blocks of $[\text{EuCl}_2(\text{H}_2\text{O})_6]\text{Cl}$.

S3. Refinement

The positions of all hydrogen atoms were identified from the difference Fourier map and were freely refined, applying one common isotropic displacement parameter to all six H atoms.

For better comparability of our structure model with the previous model by Lepert *et al.* (1983) we have used the same setting in space group $P2_1/n$. In the crystal structure description given by Lepert *et al.* (1983) several misspellings of the atomic positions were adopted into the databases. The published model leads to diverging refinements if taken as starting values. We have analysed the misspellings and give a conclusive assignment of the atomic positions. If standardized by the program *STRUCTURE-TIDY* (Gelato & Parthé, 1987), the comparison of our model with the one given by Lepert *et*

al. (1983) shows, in addition to an origin shift of (0, 1/2, 0), that the y and z coordinates of atoms O1, O2 and O3 were permuted. In fact, $y(\text{O1})$ and $z(\text{O1})$ belong to $y(\text{O3})$ and $z(\text{O3})$, $y(\text{O2})$ and $z(\text{O2})$ belong to $y(\text{O1})$ and $z(\text{O1})$, and finally $y(\text{O3})$ and $z(\text{O3})$ belong to $y(\text{O2})$ and $z(\text{O2})$. If re-ordered in the given way, the refinement based on starting values from Lepert *et al.* (1983) lead to convergence in few cycles with satisfying results.

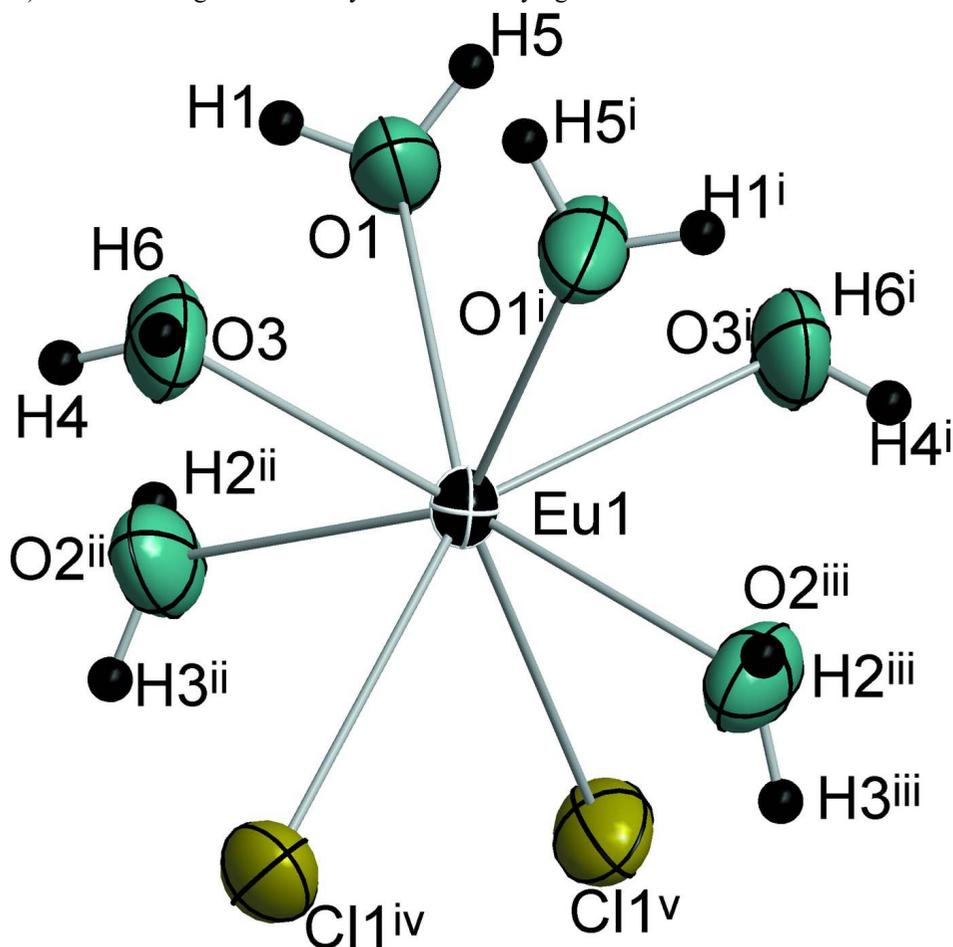
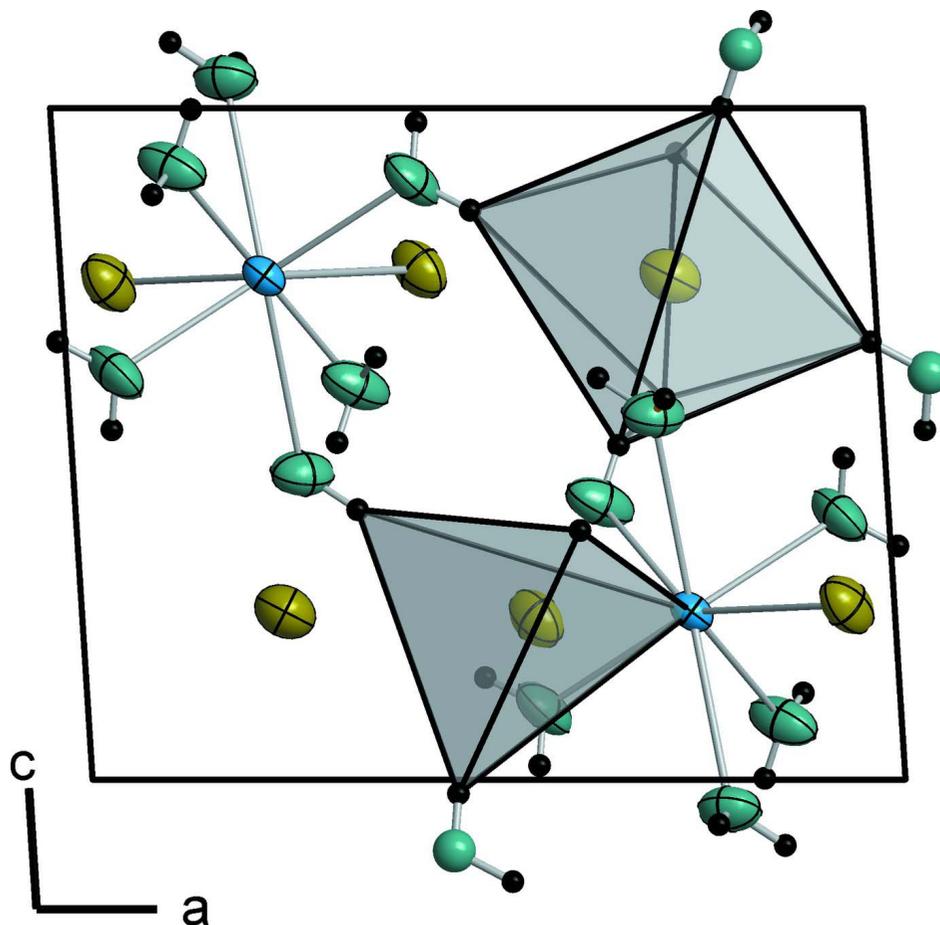


Figure 1

The cationic $[\text{Eu}(\text{H}_2\text{O})_6\text{Cl}_2]^+$ unit in $[\text{Eu}(\text{H}_2\text{O})_6\text{Cl}_2]\text{Cl}$. Ellipsoids are drawn at 75% probability level. Hydrogen atoms are drawn as small black spheres with arbitrary radius. [Symmetry code: (i) $3/2 - x, y, 1/2 - z$; (ii) $x, y, -1 + z$; (iii) $3/2 - x, y, 3/2 - z$; (iv) $1 - x, -y, 1 - z$; (v) $1/2 + x, -y, -1/2 + z$.]

**Figure 2**

View along $[010]$ on the crystal structure of $[\text{Eu}(\text{H}_2\text{O})_6\text{Cl}_2]\text{Cl}$. Small black spheres represent H atoms, blue ellipsoids represent Eu atoms, olive ellipsoids represent Cl atoms, turquoise ellipsoids represent O atoms. Grey polyhedra represent the coordination of H atoms around Cl atoms.

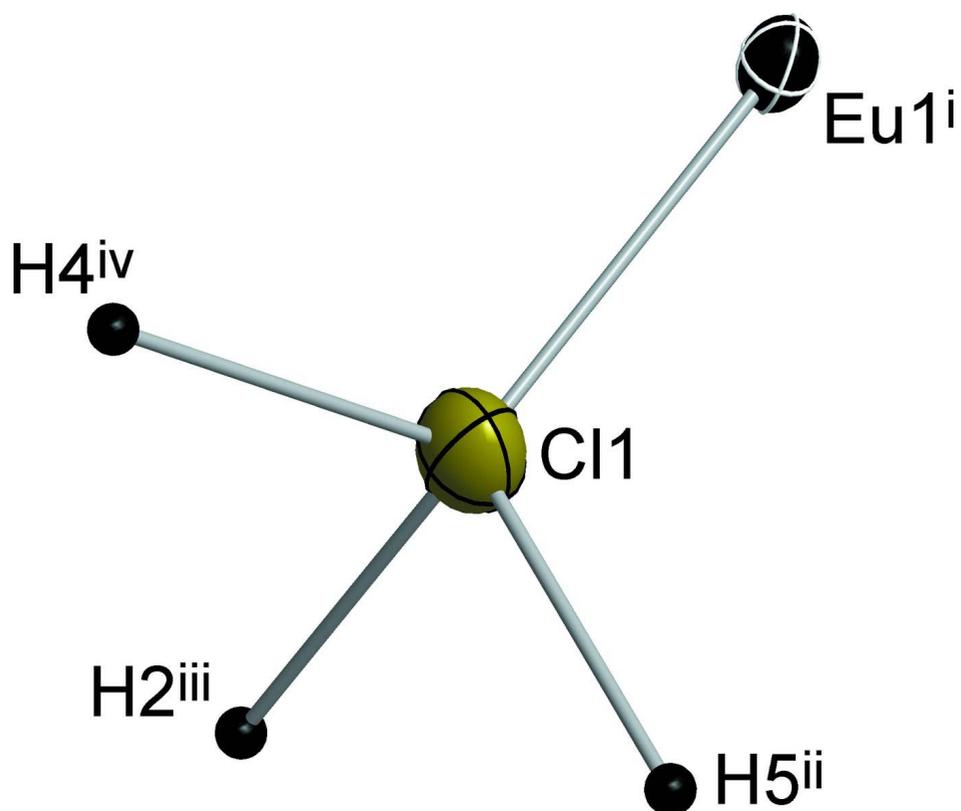


Figure 3

The coordination sphere of the coordinating C11 atom is a distorted tetrahedron built from three water molecules and one europium atom. The water molecules coordinate *via* hydrogen bonds. [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1/2 + x, 1 - y, 1/2 + z$; (iii) $3/2 - x, y, 3/2 - z$; (iv) $x, y, 1 + z$.]

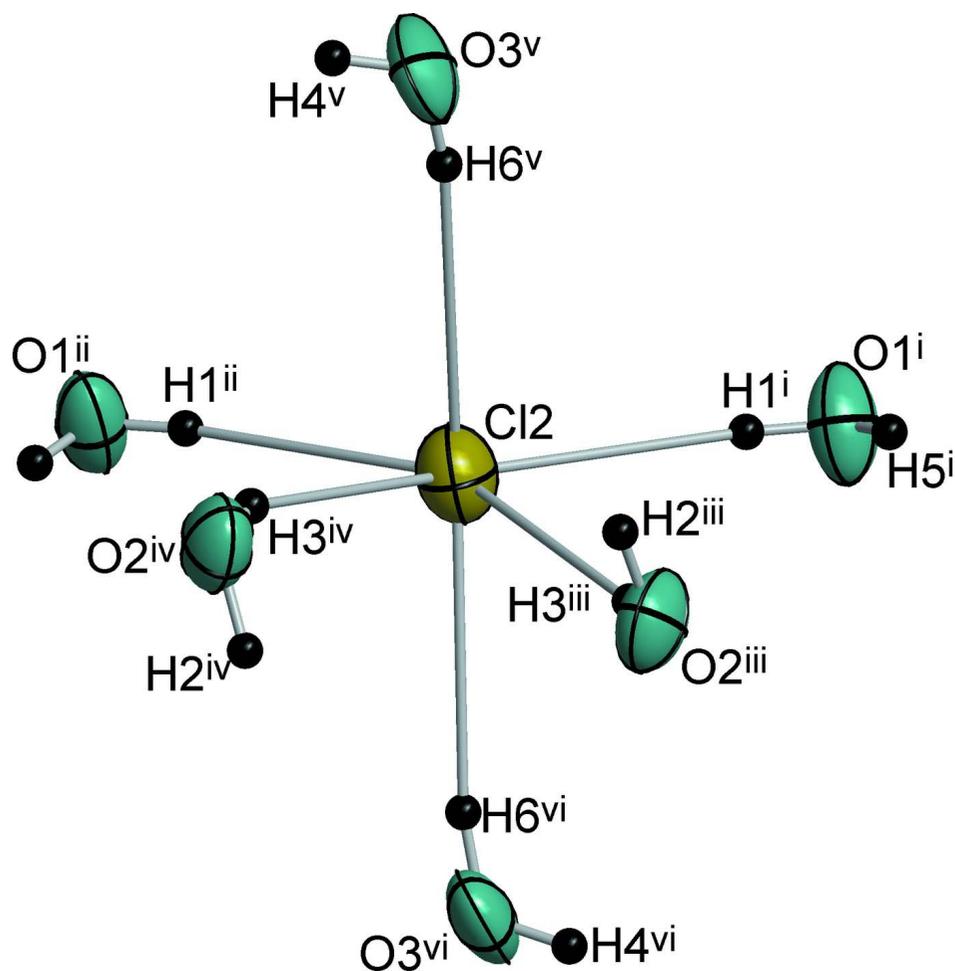


Figure 4

The coordination sphere of the anionic Cl2 atom consists of six water molecules coordinating *via* their hydrogen atoms forming a distorted octahedron. [Symmetry codes: (i) $3/2 - x, y, 1/2 - z$; (ii) $x, y, 1 + z$; (iii) $3/2 - x, 1 + y, 3/2 - z$; (iv) $x, 1 + y, z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $1/2 + x, 1 - y, 1/2 + z$.]

Hexaaquadichloridoeuropium(III) chloride

Crystal data

[EuCl₂(H₂O)₆]Cl

$M_r = 366.41$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1 yac$

$a = 9.6438 (12) \text{ \AA}$

$b = 6.5322 (10) \text{ \AA}$

$c = 7.929 (3) \text{ \AA}$

$\beta = 93.653 (13)^\circ$

$V = 498.4 (2) \text{ \AA}^3$

$Z = 2$

$F(000) = 348$

$D_x = 2.441 \text{ Mg m}^{-3}$

Ag $K\alpha$ radiation, $\lambda = 0.56083 \text{ \AA}$

Cell parameters from 13548 reflections

$\mu = 3.74 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Stretched cuboid, clear colourless

$0.23 \times 0.20 \times 0.18 \text{ mm}$

Data collection

Stoe IPDS I diffractometer	13401 measured reflections
Radiation source: fine-focus sealed tube	1762 independent reflections
Graphite monochromator	1653 reflections with $I > 2\sigma(I)$
φ scan	$R_{\text{int}} = 0.043$
Absorption correction: multi-scan (<i>MulScanAbs</i> in <i>PLATON</i> ; Spek, 2009)	$\theta_{\text{max}} = 25.5^\circ$, $\theta_{\text{min}} = 3.0^\circ$
$T_{\text{min}} = 0.425$, $T_{\text{max}} = 0.510$	$h = -14 \rightarrow 14$
	$k = -10 \rightarrow 10$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.015$	All H-atom parameters refined
$wR(F^2) = 0.032$	$w = 1/[\sigma^2(F_o^2) + (0.015P)^2]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
1762 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
66 parameters	$\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.77 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
Eu1	0.7500	0.150918 (18)	0.2500	0.01345 (3)
Cl1	0.44156 (5)	0.16532 (7)	0.76010 (6)	0.02588 (9)
Cl2	0.7500	0.62387 (11)	0.7500	0.02813 (13)
O1	0.85427 (18)	0.4256 (2)	0.0872 (2)	0.0275 (3)
O2	0.78164 (18)	0.0484 (2)	0.9561 (2)	0.0263 (3)
O3	0.56055 (17)	0.3002 (2)	0.1060 (2)	0.0278 (3)
H1	0.827 (4)	0.454 (6)	0.001 (5)	0.051 (4)*
H2	0.846 (3)	0.084 (5)	0.902 (4)	0.035 (3)*
H3	0.766 (4)	-0.063 (7)	0.933 (5)	0.058 (5)*
H4	0.551 (4)	0.265 (6)	0.020 (5)	0.052 (5)*
H5	0.881 (4)	0.520 (5)	0.129 (5)	0.040 (3)*
H6	0.491 (4)	0.319 (6)	0.152 (5)	0.044 (4)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Eu1	0.01398 (5)	0.01346 (5)	0.01244 (6)	0.000	-0.00293 (3)	0.000

C11	0.02417 (18)	0.02396 (18)	0.0286 (2)	-0.00652 (16)	-0.00541 (16)	0.00198 (17)
C12	0.0297 (3)	0.0305 (3)	0.0235 (3)	0.000	-0.0033 (2)	0.000
O1	0.0368 (8)	0.0229 (6)	0.0214 (8)	-0.0100 (6)	-0.0085 (6)	0.0038 (5)
O2	0.0336 (7)	0.0277 (7)	0.0175 (7)	-0.0047 (6)	-0.0001 (6)	-0.0039 (5)
O3	0.0250 (6)	0.0317 (7)	0.0250 (8)	0.0067 (5)	-0.0113 (6)	-0.0028 (5)

Geometric parameters (Å, °)

Eu1—O1	2.4618 (15)	O2—H3	0.76 (4)
Eu1—O1 ⁱ	2.4618 (16)	O2—H2	0.81 (3)
Eu1—O2 ⁱⁱ	2.4620 (18)	O3—H4	0.72 (4)
Eu1—O2 ⁱⁱⁱ	2.4620 (18)	O3—H6	0.79 (4)
Eu1—O3	2.3078 (16)	C11—H2	2.535 (4)
Eu1—O3 ⁱ	2.3078 (15)	C11—H4	2.3535 (4)
Eu1—C11 ^{iv}	2.7690 (12)	C11—H5 ^{vi}	2.36 (3)
Eu1—C11 ^v	2.7690 (12)	C12—H1 ⁱ	2.36 (4)
O1—H1	0.74 (4)	C12—H3 ^{vii}	2.5071 (4)
O1—H5	0.74 (4)	C12—H6 ^{viii}	2.53 (4)
Eu1—O1—H1	122 (3)	O1—Eu1—O2 ⁱⁱ	67.83 (6)
Eu1—O1—H1	122 (3)	O1 ⁱ —Eu1—C11 ^{iv}	105.35 (5)
Eu1—O1—H5	121 (3)	O1—Eu1—C11 ^{iv}	145.35 (4)
Eu1—O1—H5	121 (3)	O2 ⁱⁱ —Eu1—O2 ⁱⁱⁱ	148.45 (8)
Eu1 ^{ix} —O2—H2	124 (3)	O2 ⁱⁱ —Eu1—C11 ^{iv}	83.83 (4)
Eu1 ^{ix} —O2—H2	124 (3)	O2 ⁱⁱⁱ —Eu1—C11 ^{iv}	72.65 (4)
Eu1 ^{ix} —O2—H3	117 (3)	O3 ⁱ —Eu1—O1 ⁱ	76.70 (6)
Eu1 ^{ix} —O2—H3	117 (3)	O3—Eu1—O1 ⁱ	67.31 (6)
Eu1—O3—H4	112 (3)	O3 ⁱ —Eu1—O2 ⁱⁱ	116.15 (7)
Eu1—O3—H4	112 (3)	O3—Eu1—O2 ⁱⁱ	77.82 (6)
Eu1—O3—H6	120 (3)	O3 ⁱ —Eu1—O3	130.01 (8)
Eu1—O3—H6	120 (3)	O3 ⁱ —Eu1—C11 ^{iv}	146.64 (4)
O1 ⁱ —Eu1—O1	86.43 (9)	O3—Eu1—C11 ^{iv}	78.18 (5)
O1 ⁱ —Eu1—O2 ⁱⁱ	140.68 (5)	C11 ^{iv} —Eu1—C11 ^v	83.51 (2)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...C12 ⁱⁱ	0.74 (4)	2.36 (4)	3.081 (2)	166.08
O2—H2...C11 ⁱⁱⁱ	0.81 (3)	2.54 (3)	3.351 (2)	174.97
O2—H3...C12 ^x	0.76 (4)	2.51 (4)	3.2234 (19)	157.37
O3—H4...C11 ⁱⁱ	0.72 (4)	2.35 (4)	3.036 (2)	160.44
O1—H5 ^{vi} ...C11	0.74 (2)	2.36 (3)	3.095 (2)	173.89
O3—H6...C12 ^{viii}	0.79 (4)	2.53 (4)	3.310 (2)	170.66

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