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Hexaaqua[μ-di-μ-oxo-bis(hydroxodioxoiodate)]dieuropium(III) bis(perchlorate) dihydrate

Andreas Fischer

Inorganic Chemistry, School of Chemical Science and Engineering, Royal Institute of Technology, 100 44 Stockholm, Sweden

Correspondence e-mail: andif@inorg.kth.se

Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(I–O) = 0.005 Å
H-atom completeness 12%
R factor = 0.031
wR factor = 0.077
Data-to-parameter ratio = 22.1

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

The title compound, $[Eu_2(H_2I_2O_{10})(H_2O)_6](ClO_4)_2\cdot 2H_2O$, is isostructural with the corresponding Pr, Sm and Gd phases. It features Eu^{3+} cations, which are coordinated by centrosymmetric $H_2I_2O_{10}^{4-}$ anions and water molecules, forming positively charged sheets, separated by perchlorate anions and non-coordinated water molecules.

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Comment

The structural and coordination chemistry of periodate species is complicated by the fact that they can appear as tetrahedral IO_4^- anions, and also as octahedral anions, which can be derived from periodic acid, H_5IO_6. The latter can dimerize by condensation, yielding species such as $H_4I_2O_{10}^{2-}$ and $H_2I_2O_{10}^{4-}$. We decided to investigate the lanthanide(III)/oxohalogenate system more thoroughly, starting with the oxoiodates.

From solutions of gadolinium perchlorate and samarium perchlorate, respectively, and periodic acid, single crystals of a novel lanthanide perchlorate diperiodate could be isolated and structurally characterized (Fischer, 2003*a*). From similar solutions containing praseodymium perchlorate, three different polymorphs of praseodymium perchlorate diperiodate could be obtained (Fischer, 2004). Combining solutions of europium perchlorate and periodic acid yielded single crystals of the title compound, (I) (Fig. 1), which is isostructural with the α-Pr structure as well as with the Sm and Gd compounds.

The Eu^{3+} cation in (I) is coordinated by three $(H_2I_2O_{10})^{4-}$ periodate anions (two bidentate and one monodentate). Its

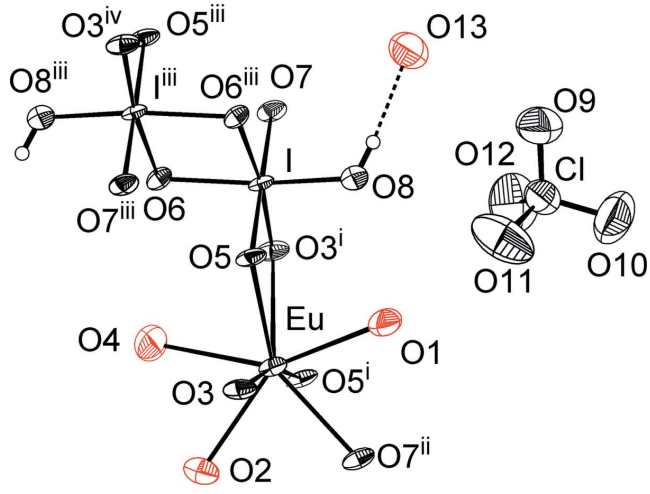

Figure 1
The structural units in (I), shown with 80% displacement ellipsoids (arbitrary spheres for H atoms). Water O atoms are drawn in red. Symmetry codes are as in Table 1; additionally, (iv) $x, -y-\frac{1}{2}, z+\frac{1}{2}$.

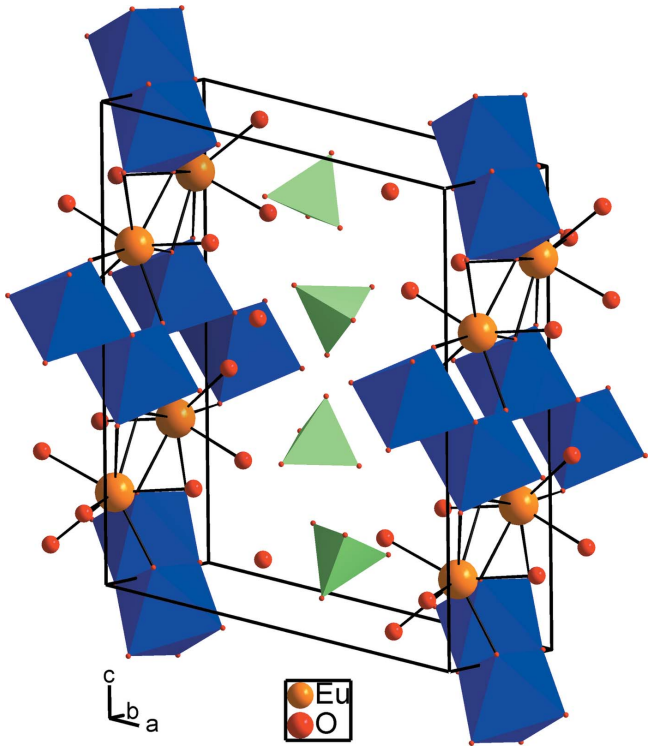

Figure 2
The unit-cell contents of (I), viewed down [010]. Colour key: blue polyhedra $H_2I_2O_{10}^{4-}$ and green polyhedra: ClO_4^-.

coordination is completed by three water molecules, yielding a distorted bicapped trigonal prism. The average Eu—O bond length (2.431 Å) is larger than in both the respective Sm and Gd compounds (Sm: 2.428 Å; Gd: 2.399 Å), which is not consistent with the lanthanide contraction trend (decreasing ionic radii towards the heavier elements).

The geometry of the $(H_2I_2O_{10})^{4-}$ anion in (I), which has $\overline{1}$ site symmetry about the mid-point between the I atoms, is essentially the same as in the isostructural Pr, Sm and Gd compounds. One water molecule of crystallization is bonded to the anion *via* an O8—H8···O13 hydrogen bond [H···O = 1.88 Å, O···O = 2.645 (5) Å and O—H···O = 173°]. The presence of short O···O contacts suggests the existence of further hydrogen bonds in (I), but the water H atoms were not located in the present study.

Experimental

A 1 *M* europium(III) perchlorate solution was prepared from europium oxide (AlfaAesar, 99.9%) and perchloric acid (Fluka, 70%). An excess of 10% of the acid was used to facilitate complete dissolution. A 1 *M* solution of periodic acid was prepared by dissolving the purchased material (Aldrich, 99.999%). Small volumes (1 ml) of each solution were mixed in an NMR tube, which was kept in a normal laboratory atmosphere for evaporation. After one year, isometric crystals of $Eu_2(H_4IO_6)(I_2O_{10})\cdot H_3O\cdot 5H_2O$ (isostructural with its Pr, Nd and Sm analogues; Fischer, 2003*b*) had formed. After another year, plate-shaped colourless crystals of (I) could be isolated. Caution: all perchlorates are potentially explosive and all appropriate safety precautions should be followed when handling such materials.

Crystal data

$[Eu_2(H_2I_2O_{10})(H_2O)_6]$-$(ClO_4)_2\cdot 2H_2O$	D_x = 3.348 Mg m^{-3}
M_r = 531.38	Ag $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 17576 reflections
a = 10.8602 (4) Å	θ = 4.1–23.6°
b = 7.1828 (3) Å	μ = 4.88 mm^{-1}
c = 13.7933 (5) Å	T = 299 K
β = 101.584 (2)°	Plate, colourless
V = 1054.05 (7) Å^3	0.12 × 0.07 × 0.04 mm
Z = 4	

Data collection

Bruker–Nonius KappaCCD diffractometer	3211 independent reflections
ω and φ scans	2723 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (*HABITUS*; Herrendorf & Bärnighausen, 1997)	R_{int} = 0.060
T_{min} = 0.593, T_{max} = 0.866	θ_{max} = 23.6°
17576 measured reflections	h = −15 → 15
	k = −10 → 10
	l = −19 → 19

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 3.015P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.077	$\Delta\rho_{max}$ = 1.84 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −1.65 e Å^{-3}
3211 reflections	
145 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Eu—O5^{i}	2.357 (3)	Eu—O3^{i}	2.518 (3)
Eu—O7^{ii}	2.402 (3)	I—O7	1.820 (3)
Eu—O1	2.404 (4)	I—O3^{i}	1.844 (3)
Eu—O2	2.413 (3)	I—O5	1.859 (3)
Eu—O3	2.417 (3)	I—O8	1.868 (3)
Eu—O4	2.455 (4)	I—O6	1.955 (3)
Eu—O5	2.478 (3)	I—O6^{iii}	1.974 (3)
I—O6—I^{iii}	101.36 (13)		

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

Only the H atom on the $H_2I_2O_{10}$ anion could be located in a difference map. It was refined as riding (O—H = 0.77 Å), with $U_{iso}(H) = 1.2U_{eq}(O)$. The maximum and minimum electron-density peaks are located 0.90 and 0.60 Å, respectively, from the Eu atom.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *MAXUS* (Mackay *et al.*, 1999).

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