Cerium triiodate, Ce(IO$_3$)$_3$

Xue-An Chen,* Li Zhang, Xin-An Chang, He-Gui Zang and Wei-Qiang Xiao

College of Materials Science and Engineering, Beijing University of Technology, Ping Le Yuan 100, Beijing 100022, People's Republic of China

Correspondence e-mail: xu_jiang_2002@yahoo.com

The crystal structure of Ce(IO$_3$)$_3$ consists of one-dimensional chains of edge-sharing CeO$_9$ polyhedra which are crosslinked into two-dimensional layers through bridging IO$_3^-$ groups. The layers are held together *via* long I$\cdots$O contacts, resulting in an extended three-dimensional network. The I—O bond distances and O—I—O angles are normal, lying in the ranges 1.806 (4)–1.846 (4) Å and 89.9 (2)–100.9 (2)°, respectively. The three crystallographically independent iodate groups all show different coordination modes.

Comment

Metal iodates are of considerable interest because some of these compounds exhibit piezoelectric and pyroelectric effects, and they have potential applications in second-harmonic generation (Morosin *et al.*, 1973). Ce(IO$_3$)$_3$ was previously synthesized by Abrahams *et al.* (1976), who predicted it to be isostructural with Gd(IO$_3$)$_3$ (Liminga *et al.*, 1977), in space group $P2_1/a$, with a = 13.56 (2) Å, b = 8.565 (9) Å, c = 7.214 (12) Å, β = 99.7 (3)° and V = 826 (2) Å^3. Recently, Douglas *et al.* (2004) re-investigated the rare earth iodates and reported the lattice constants of all anhydrous 4f-iodates, except for those of Ce(IO$_3$)$_3$. They found that Ln(IO$_3$)$_3$ compounds (Ln is Pr, Nd, Sm, Eu, Gd, Tb, Ho or Er) crystallize in a Gd(IO$_3$)$_3$-type structure. In the course of our research on novel iodate non-linear optical (NLO) materials, we have obtained single crystals of Ce(IO$_3$)$_3$. Our X-ray structural analysis indicated that the newly prepared Ce(IO$_3$)$_3$ is a new polymorph, with cell dimensions different from those given by Abrahams *et al.* We report the crystal structure here.

In the structure of Ce(IO$_3$)$_3$, each Ce^{3+} ion is coordinated to nine O atoms in a distorted monocapped square-antiprismatic geometry, as shown in Fig. 1. The Ce—O distances of 2.420 (4)–2.809 (5) Å (average 2.556 Å; Table 1) are very reasonable when compared with the ranges 2.427 (3)–2.803 (3) Å (average 2.536 Å) in Ce$_2$(SO$_4$)$_3$·5H$_2$O (Junk *et al.*, 1999) and 2.496 (3)–2.519 (3) Å (average 2.511 Å) in Ce-(HSO$_4$)$_3$ (Wickleder, 1998), all featuring nine-coordinate Ce.

The CeO$_9$ polyhedra share edges with each other to form zigzag chains parallel to the b axis (Fig. 2). There are two sets of Ce$\cdots$Ce distances within the chains, *viz*. 4.2878 (7) and 4.5070 (7) Å. The longer Ce$^i\cdots$Ce^{ii} contacts are associated with pairs of Ce atoms double-bridged through I3O$_3^-$ groups (sharing the O9$\cdots$O9^{iii} edge), while the shorter ones (Ce$\cdots$Ce^i) are those involved in the two bridging I2O$_3^-$ and two bridging I3O$_3^-$ groups (sharing the O6$\cdots$O6^i edge) [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 2 - y, 1 - z$]. These chains are crosslinked by I1O$_3^-$ groups *via* μ_2-bridging O atoms, resulting in a two-dimensional layer parallel to the (101) plane. Adjacent layers are further connected together through long I$\cdots$O contacts [I2$\cdots$O2 = 2.779 (5) Å, I2$\cdots$O5 = 2.390 (5) Å, I3$\cdots$O2 = 2.738 (5) Å and I3$\cdots$O7 = 2.851 (5) Å], giving rise to an extended three-dimensional network.
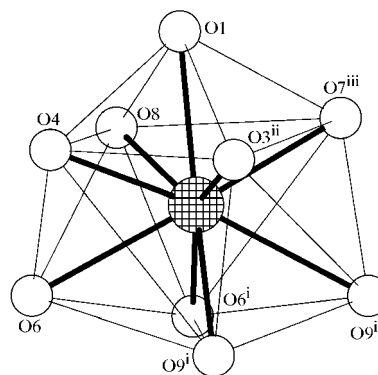

Figure 1
The coordination geometry about the Ce atom. The double-shaded circle denotes a Ce atom and open circles denote O atoms. The monocapped square antiprism is indicated by thin lines. See Table 1 for symmetry codes.
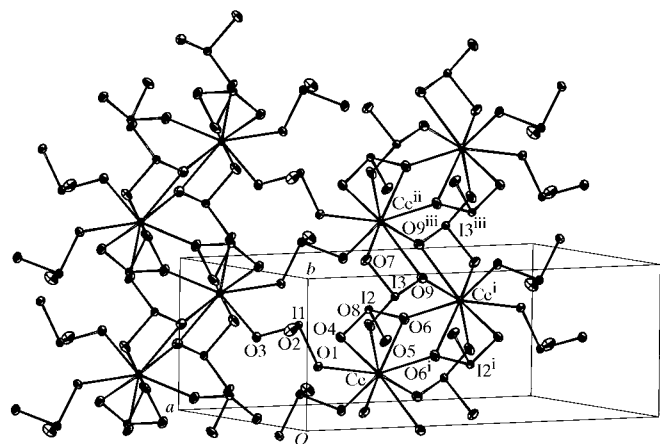

Figure 2
The Ce(IO$_3$)$_3$ layer parallel to the (101) plane, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $x, 1 + y, z$; (iii) $1 - x, 2 - y, 1 - z$.]

inorganic compounds

There are three crystallographically unique iodate groups, which adopt different coordination modes toward Ce^{3+} ions (Fig. 2). Each $I1O_3^-$ group is a bidentate ligand bonded to two Ce^{3+} centres *via* two μ_2-O atoms, each $I2O_3^-$ group functions as a tridentate ligand, chelating one Ce^{3+} and coordinated to a second Ce^{3+} ion through a μ_3-O atom, while each of the $I3O_3^-$ groups acts as a tetradentate ligand that chelates one Ce^{3+} centre and simultaneously binds the other two *via* a μ_2-O and a μ_3-O atom, respectively. Despite the difference in the coordination schemes of the iodate groups, the I—O bond lengths of 1.806 (4)–1.846 (4) Å and the O—I—O angles of 89.9 (2)–100.9 (2)° show no particular distortions and are within the ranges observed previously for inorganic iodates (Douglas *et al.*, 2004). Bond-valence-sum (Brown & Altermatt, 1985) calculations give values of 3.14 for Ce and 4.74–4.93 for I atoms, in reasonable agreement with their expected formal valences.

The crystal structure of $Ce(IO_3)_3$ presented here is different from that previously reported by Abrahams *et al.* (1976). The latter contains a three-dimensional network consisting of irregular CeO_8 polyhedra bridged by bi- and tridentate IO_3^- ligands. It is the difference in the coordination modes of the iodate groups, as well as the variation in the Ce^{3+} coordination geometry, that is responsible for the structural versatility of $Ce(IO_3)_3$.

Experimental

The title compound was synthesized using hydrothermal techniques. All reagents were of analytical grade. $Ce(NO_3)_3 \cdot 6H_2O$ (0.106 g, 0.244 mmol), I_2O_5 (0.287 g, 0.860 mmol) and H_2O (5 ml) were sealed in a 25 ml Teflon-lined autoclave. This was heated in an oven at 443 K for one week under autogenously generated pressure, then cooled slowly to room temperature. The product consisted of yellow block-shaped crystals, with largest dimensions of $0.6 \times 0.8 \times 1.0$ mm, covered by a colourless liquid. The final pH of the reaction system was about 1.0. The crystals were isolated in about 84% yield (based on Ce) by washing the reaction product with deionized water and anhydrous ethanol, followed by drying with anhydrous acetone. Powder X-ray diffraction analysis revealed that the product is a single phase of $Ce(IO_3)_3$ and no lines due to impurity phases were observed. In previous work (Douglas *et al.*, 2004), $Ln(IO_3)_3$ compounds (Ln is Pr, Nd, Sm, Eu, Gd, Tb, Ho or Er) were prepared by decomposition of the corresponding periodates under hydrothermal conditions. Here, the Ce analogue was synthesized directly from the hydrothermal reaction of $Ce(NO_3)_3$ with I_2O_5. I_2O_5 was found to play an important role in the crystal growth of $Ce(IO_3)_3$. The replacement of I_2O_5 by H_5IO_6 as an iodine source did not generate any crystalline products, instead forming lumps of amorphous gel.

Crystal data

$Ce(IO_3)_3$	$D_x = 5.431$ Mg m^{-3}
$M_r = 664.82$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 8.9188$ (10) Å	reflections
$b = 5.9619$ (11) Å	$\theta = 16.8$–22.5°
$c = 15.4047$ (12) Å	$\mu = 17.01$ mm^{-1}
$\beta = 96.974$ (8)°	$T = 290$ K
$V = 813.05$ (19) Å^3	Plate, yellow
$Z = 4$	$0.10 \times 0.08 \times 0.05$ mm

Table 1
Selected geometric parameters (Å).

Ce—O6^i	2.420 (4)	Ce—O7^{iii}	2.529 (5)
Ce—O3^{ii}	2.480 (4)	Ce—O4	2.567 (4)
Ce—O8	2.485 (4)	Ce—O6	2.700 (5)
Ce—O9^i	2.506 (4)	Ce—O9^{iii}	2.809 (5)
Ce—O1	2.507 (4)		

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

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.043$
$2\theta/\omega$ scans	$\theta_{max} = 35.0°$
Absorption correction: ψ scan	$h = 0 \rightarrow 14$
(Kopfmann & Huber, 1968)	$k = 0 \rightarrow 9$
$T_{min} = 0.201$, $T_{max} = 0.420$	$l = -24 \rightarrow 24$
4133 measured reflections	3 standard reflections
3582 independent reflections	every 150 reflections
3317 reflections with $I > 2\sigma(I)$	intensity variation: $\pm 1.7\%$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$\Delta\rho_{max} = 2.86$ e Å^{-3}
$wR(F^2) = 0.087$	$\Delta\rho_{min} = -2.67$ e Å^{-3}
$S = 1.17$	Extinction correction: *SHELXL97*
3582 reflections	(Sheldrick, 1997)
119 parameters	Extinction coefficient: 0.0060 (2)
$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2$	
$+ 9.4569P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Direct phase determination yielded the positions of the Ce and I atoms. The remaining O atoms were located in subsequent difference Fourier syntheses. All atoms were refined anisotropically. The highest residual electron-density peaks were located 0.69 Å from the Ce atoms.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1994); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *Rigaku/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SCHAKAL92* (Keller, 1992); software used to prepare material for publication: *SHELXL97*.

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