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$Cu_3Er(SeO_3)_2O_2Cl$, the Erbium Analogue of Francisite

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Abstract

The title compound, tricopper erbium chloride bis(oxide) bis[trioxoselenate(2−)], consists of an infinite three-dimensional framework of cations and O atoms, and contains eight-coordinate Er^{3+}, square-planar Cu^{2+} and three-coordinate Se^{4+} ions. The Cl ions and the Se lone pair of electrons occupy tunnels parallel to [001]. The mean bond distances are: Er—O 2.38 (8), Cu1—O (in the square plane) 1.96 (7), Cu1—Cl (out of plane) 3.015 (2), Cu2—O 1.95 (3), Cu2—Cl 3.1753 (9) and Se—O 1.696 Å. The shortest Cu···Cu distance is 3.150 Å and the shortest O···O distance is 2.48 Å (O3···O3).

Comment

Following the determination of the structure of francisite, $Cu_3Bi(SeO_3)_2O_2Cl$ (Pring, Gatehouse & Birch, 1990), experiments were carried out to substitute lanthanide ions for Bi^{3+}. The structure of $Cu_3Er(SeO_3)_2O_2Cl$ is depicted in Fig. 1 and consists of an infinite three-dimensional framework of cations and O atoms containing eight-coordinate Er^{3+}, four-coordinate Cu^{2+} and three-coordinate Se^{4+} ions. The coordination of each ion is illustrated in Fig. 2. Cl^- ions and the lone pair of electrons of Se occupy tunnels within the framework parallel to [001], as in francisite.

The Er^{3+}-ion coordination sphere is best described as an 8,14,8-D_{2h} polyhedron, using the method of King (1970), in which the numbers refer to the number of vertices, edges and faces of the polyhedron, respectively.

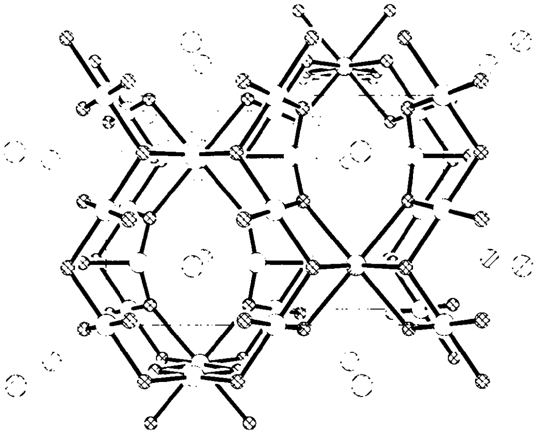

Fig. 1. *SHELXTL-Plus* (Sheldrick, 1991) diagram of $Cu_3Er(SeO_3)_2O_2Cl$ viewed along [001]. Striped spheres represent Cl atoms and cross-hatched spheres O atoms.

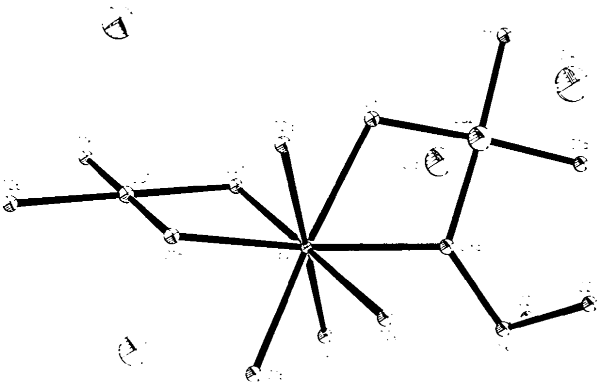

Fig. 2. *SHELXTL-Plus* (Sheldrick, 1991) diagram showing the O and Cl coordination of the Er, Cu1, Cu2 and Se ions. Lower case letters in atom numbers correspond to the symmetry transformations indicated here: (*a*) $x, y, z-1$; (*b*) $x, \frac{1}{2}-y, z-1$; (*c*) $-x, 1-y, 1-z$; (*d*) $\frac{1}{2}+x, y-\frac{1}{2}, 1-z$; (*e*) $\frac{1}{2}+x, 1-y, 1-z$; (*f*) $-x, y-\frac{1}{2}, 1-z$; (*g*) $x, \frac{1}{2}-y, z$; (*h*) $-x, -y, 1-z$; (*i*) $x, y-1, z$; (*j*) $-x, 1-y, -z$; (*k*) $1-x, 1-y, 1-z$; (*l*) $\frac{1}{2}-x, y, z$.

While the Er polyhedron is formally of the same type as that of Bi in francisite, the bond lengths differ. For Bi in francisite the Bi—O bonds range from 2.23 (2) to 2.80 (2) Å for eightfold coordination (mean 2.48 Å), and from 2.23 (2) to 2.45 (1) Å for sixfold coordination [mean 2.38 (11) Å].* In the Er compound, the Er—O bonds range from 2.27 (1) to 2.50 (1) Å for eight-coordination (mean 2.38 (9) Å), and from 2.271 (9) to 2.380 (7) Å [mean 2.34 (6) Å] for six-coordination.

Abrahams, Jamieson & Bernstein (1967) show that in seven compounds, six Bi atoms have six Bi—O bonds less than 2.68 Å and a further two Bi atoms have five Bi—O bonds also less than 2.68 Å, the overall average Bi—O bond being 2.37 Å.

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* For mean bond distances the numbers in parentheses are standard deviations, for bond lengths these numbers are standard uncertainties.

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The Cu^{2+} ions have square-planar coordination geometry. The Cu1—O bonds range from 1.897 (5) to 2.025 (7) Å, and the Cu2—O bonds range from 1.922 (9) to 1.972 (10) Å. Both Cu ions have Cu···Cl contacts: Cu1···Cl 2 × 3.015 (2), Cu2···Cl 2 × 3.1753 (9) Å. The copper–oxygen square planes have O1 in common, linking them into zigzag chains parallel to [001].

The Se^{4+} ions are three-coordinate (with triangular pyramidal coordination geometry) with a mean Se—O bond length of 1.696 Å. The position of the lone pair of electrons is essentially as in francisite (Pring, Gatehouse & Birch, 1990). The shortest O···O contacts are given in Table 2.

The bond-valence sums (Brown & Altermatt, 1985) are Cu1 1.90, Cu2 1.94, Er 2.84 and Se 4.09 v.u., and the O atoms have a mean bond-valence sum of 2.09 v.u.

Experimental

Bright green crystals of the Er^{3+} compound were obtained by mixing Er_2O_3 (0.5 g), CuO (0.52 g), $CuCl_2.2H_2O$ (0.22 g) and SeO_2 (0.58 g) in a teflon-lined stainless steel hydrothermal bomb. The bomb was heated in a furnace for 5 d at 473 K then cooled slowly to room temperature over 24 h. The La^{3+} (pale blue) and Nd^{3+} (green) compounds were obtained as powders.

Crystal data

$Cu_3Er(SeO_3)_2O_2Cl$
$M_r = 679.27$
Orthorhombic
Pmmn
$a = 6.299\,(1)$ Å
$b = 9.432\,(3)$ Å
$c = 6.967\,(2)$ Å
$V = 413.92\,(2)$ Å^3
$Z = 2$
$D_x = 5.45$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 6$–$16°$
$\mu = 26.97$ mm^{-1}
$T = 293.0\,(10)$ K
Tabular
0.075 × 0.0625 × 0.0125 mm
Green

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: from crystal shape (*SHELXTL-Plus*; Sheldrick, 1991)
$T_{min} = 0.323$, $T_{max} = 0.715$
744 measured reflections

744 independent reflections
482 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 30°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.034$
$wR = 0.039$
$S = 0.98$
482 reflections
46 parameters
$w = 1/[\sigma^2(F) + 0.0096F^2]$
$(\Delta/\sigma)_{max} = 0.015$

$\Delta\rho_{max} = 2.17$ e Å^{-3} (close to Er)
$\Delta\rho_{min} = -1.98$ e Å^{-3} (close to Er)
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.3.1 and 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Er	1/4	1/4	0.2655 (1)	0.0042 (2)
Cu1	0	0	0	0.0087 (4)
Cu2	1/4	1/4	0.7949 (3)	0.0080 (6)
Se	1/4	0.5606 (1)	0.5900 (2)	0.0068 (4)
O1	1/4	0.1122 (10)	0.9981 (13)	0.007 (2)
O2	0.0393 (12)	0.5876 (7)	0.7371 (10)	0.0134 (18)
O3	1/4	0.1188 (10)	0.5745 (14)	0.010 (3)
Cl	1/4	3/4	0.1472 (9)	0.0267 (18)

Table 2. *Selected geometric parameters (Å)*

Er—O1^{i,ii}	2.271 (9)	Cu2—Cl^{xi,iii}	3.1753 (9)
Er—O2^{iii,iv,v,vi}	2.380 (7)	Se—O2^{xii,vii}	1.696 (7)
Er—O3^{vii}	2.484 (10)	Se—O3^{vii}	1.696 (10)
Cu1—O1^{i,viii}	1.897 (5)	Cu1—Cu1^{xiii,xiv}	3.150
Cu1—O2^{iv,ii}	2.025 (7)	Cu1—Cu2^{i,viii}	3.175 (1)
Cu1—Cl^{ix,x}	3.015 (2)	O1—O1^{vii}	2.60 (2)
Cu2—O1^{vii}	1.922 (9)	O2—O1^{xv}	2.60 (1)
Cu2—O3^{vii}	1.972 (10)	O3—O3^{vii}	2.48 (2)

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

The θ scan width was $(1.3 + 0.3\tan\theta)°$ from the calculated Bragg angle. Measurements were made using a scan speed of 0.04° min^{-1} and background counts were collected for 50% of the scan time on each side of every scan.

Data collection: Philips PW1100 software. Cell refinement: Philips PW1100 software. Data reduction: Philips PW1100 software. Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELX*76. Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1088). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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