References

Effenberger, H. (1985). *Z. Kristallogr.* **173**, 267–272.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Gospodinov, G. G. & Barkov, D. (1991). *Z. Phys. Chem.* **171**, 241–247.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Killean, R. C. G. & Lawrence, J. L. (1969). *Acta Cryst.* B**25**, 1750–1752.
Kohn, K., Inoue, K., Horie, O. & Akimoto, S.-I. (1976). *J. Solid State Chem.* **18**, 27–37.
Koskenlinna, M. & Valkonen, J. (1995). *Acta Cryst.* C**51**, 1–3.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Valkonen, J. (1994*a*). *Acta Cryst.* C**50**, 991–994.
Valkonen, J. (1994*b*). *Acta Cryst.* C**50**, 1381–1384.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1996). C**52**, 493–496

Hydrazinium(1+) Hexafluorogallate(III) and Hydrazinium(2+) Aquapentafluorogallate(III)

ANTON MEDEN, JOŽE ŠIFTAR AND LJUBO GOLIČ

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva 5, POB 537, 61001 Ljubljana, Slovenia

(*Received 19 May 1995; accepted 14 August 1995*)

Abstract

$(N_2H_5)_3[GaF_6]$ contains GaF_6^{3-} octahedra arranged in a distorted cubic close-packed manner and linked to hydrazinium(1+) ions *via* N—H···F hydrogen bonds. $(N_2H_6)[GaF_5(H_2O)]$ contains $[GaF_5(H_2O)]^{2-}$ octahedra arranged in a similar distorted cubic close-packed manner; in addition to N—H···F hydrogen bonds to hydrazinium(2+) ions, these octahedra are also linked directly *via* O—H···F hydrogen bonds.

Comment

The structures studied here are those of two members of the family of hydrazinium(1+) [hydrazinium(1+) hexafluorogallate, (I)] or -(2+) [hydrazinium(2+) aquapentafluorogallate, (II)] fluorometallates of main Group III metals. Compounds in this family for which the structures are known are $N_2H_5[BF_4]$ (Conant & Roof, 1970), $N_2H_6[BF_4]_2$ (Frlec, Gantar, Golič & Leban, 1984) and $(N_2H_{5.5})_2[GaF_6].2H_2O$ (Meden, Golič & Šiftar, 1992), which contain isolated fluorometallate ions, and $N_2H_5[InF_4(H_2O)]$ (Bukovec & Golič, 1976), which contains chains of complex ions. Extensive hydrogen bonding of the type N—H···F is present in all of the above. The structures of both (I) and (II) contain quite regular octahedra, which are isolated from each other and are arranged in a distorted f.c.c. fashion (see Figs. 1 and 2).

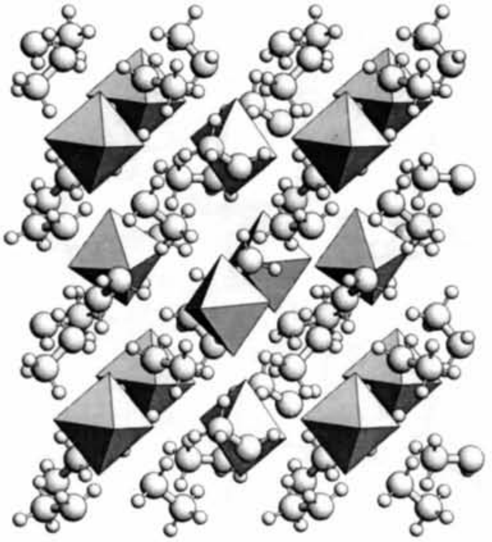

Fig. 1. *ATOMS* (Dowty, 1991) plot of the structure of $(N_2H_5)_3[GaF_6]$ showing the packing of the octahedra and positions of hydrazinium(1+) ions (more than one unit cell is shown).

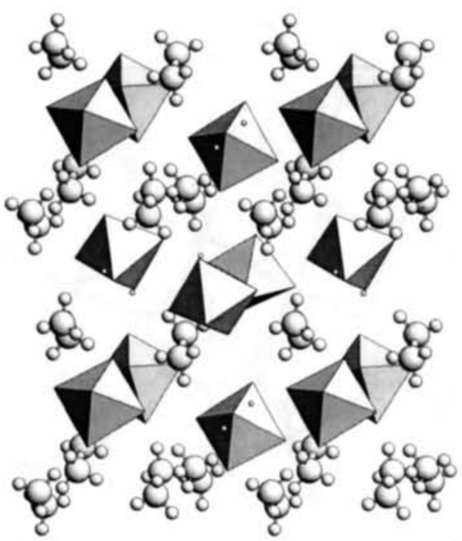

Fig. 2. *ATOMS* (Dowty, 1991) plot of the structure of $(N_2H_6)[GaF_5(H_2O)]$ showing the packing of the octahedra and positions of hydrazinium(2+) ions (more than one unit cell is shown).

The hydrogen bonding in both structures is very efficient. Every H atom, except H31 and H32 in the case of $(N_2H_5)_3[GaF_6]$ (see Fig. 3), takes part in a hydrogen bond and every F atom is hydrogen bonded to at least one N atom. N—H···N hydrogen bonds, which could also exist in $(N_2H_5)_3[GaF_6]$, are not present. In the case of $(N_2H_6)[GaF_5(H_2O)]$, there are also O—H···N bonds present between $[GaF_5(H_2O)]^{2-}$ octahedra in addition to the N—H···F hydrogen bonds (see Fig. 4). The F···N and F···O distances range from 2.58 to 2.85 Å.

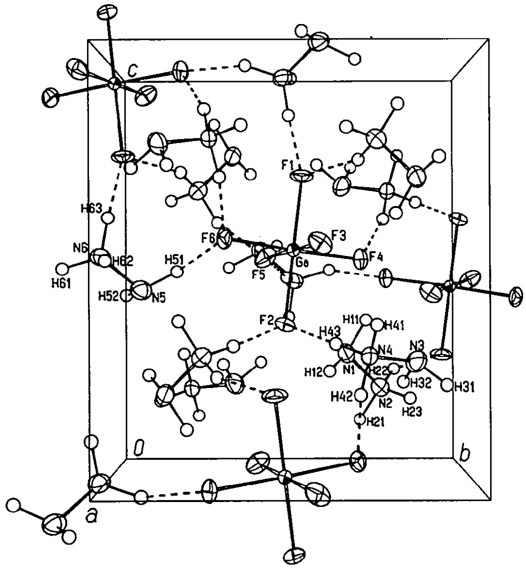

Fig. 3. *ORTEP* (Johnson, 1965) view of the unit cell of $(N_2H_5)_3[GaF_6]$ with completed structural moieties and atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

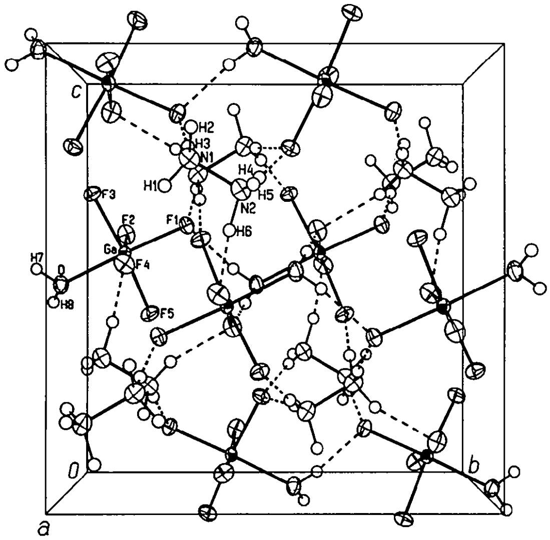

Fig. 4. *ORTEP* (Johnson, 1965) view of the unit cell of (N_2H_6)-$[GaF_5(H_2O)]$ with completed structural moieties and atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The crystals of both compounds are stable in air and were prepared by room-temperature evaporation of a solution of N_2H_4, GaF_3 and HF. Different compositions were obtained by varying the molar ratios. Details of the synthesis of $(N_2H_6)[GaF_5(H_2O)]$ are published elsewhere (Šiftar & Bukovec, 1970). The new compound $(N_2H_5)_3[GaF_6]$ was prepared by mixing aqueous solutions of N_2H_5F and GaF_3 in a molar ratio of 3:1.

Compound (I)

Crystal data

$(N_2H_5)_3[GaF_6]$
$M_r = 282.87$
Orthorhombic
$P2_12_12_1$
$a = 9.125\ (2)$ Å
$b = 9.241\ (2)$ Å
$c = 10.532\ (2)$ Å
$V = 888.1\ (3)$ Å^3
$Z = 4$
$D_x = 2.116$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 75 reflections
$\theta = 9.99$–$17.94°$
$\mu = 3.16$ mm^{-1}
$T = 293$ K
Prism
0.53 × 0.46 × 0.34 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
10 393 measured reflections
1497 independent reflections
1429 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.029$
$\theta_{\rm max} = 29.94°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
frequency: 333 min
intensity decay: 1.14%

Refinement

Refinement on F
$R = 0.033$
$wR = 0.019$
$S = 1.024$
1469 reflections
178 parameters
All H-atom parameters refined
Regina weighting scheme

$(\Delta/\sigma)_{\rm max} = 2.21$
$\Delta\rho_{\rm max} = 0.644$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.138$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

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

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

	x	y	z	$U_{\rm eq}$
Ga	0.54452 (4)	0.51246 (3)	0.54627 (3)	0.0136 (1)
F1	0.5202 (2)	0.5353 (3)	0.7256 (2)	0.030 (1)
F2	0.5724 (2)	0.4893 (3)	0.3687 (2)	0.0245 (8)
F3	0.7348 (2)	0.5851 (3)	0.5589 (2)	0.031 (1)
F4	0.4700 (3)	0.7010 (2)	0.5243 (2)	0.0279 (9)
F5	0.3550 (3)	0.4325 (3)	0.5293 (2)	0.031 (1)
F6	0.6175 (3)	0.3241 (3)	0.5730 (2)	0.034 (1)
N1	0.3050 (5)	0.6647 (4)	0.2909 (4)	0.031 (2)
N2	0.2425 (5)	0.7663 (4)	0.2003 (4)	0.026 (2)
N3	0.6772 (5)	0.8426 (5)	0.2859 (5)	0.032 (2)
N4	0.7607 (5)	0.7123 (4)	0.3007 (4)	0.026 (2)
N5	0.4937 (4)	0.0848 (4)	0.4516 (4)	0.029 (1)
N6	0.5756 (3)	−0.0145 (4)	0.5297 (3)	0.027 (1)

Table 2. *Selected geometric parameters (Å, °) for (I)*

Ga—F1	1.913 (2)	Ga—F5	1.889 (2)
Ga—F2	1.900 (2)	Ga—F6	1.885 (2)
Ga—F3	1.866 (2)	N3—N4	1.434 (6)
Ga—F4	1.884 (2)		
F1—Ga—F2	179.0 (1)	F2—Ga—F6	89.8 (1)
F1—Ga—F3	89.9 (1)	F3—Ga—F4	90.7 (1)
F1—Ga—F4	88.70 (9)	F3—Ga—F5	177.6 (1)
F1—Ga—F5	91.7 (1)	F3—Ga—F6	89.6 (1)
F1—Ga—F6	89.7 (1)	F4—Ga—F5	91.1 (1)
F2—Ga—F3	89.2 (1)	F4—Ga—F6	178.4 (1)
F2—Ga—F4	91.83 (9)	F5—Ga—F6	88.7 (1)
F2—Ga—F5	89.2 (1)		

Compound (II)

Crystal data

$(N_2H_6)[GaF_5(H_2O)]$
$M_r = 216.79$
Orthorhombic
Pbca
$a = 9.248\ (1)$ Å
$b = 10.942\ (1)$ Å
$c = 11.199\ (1)$ Å
$V = 1133.2\ (2)$ Å^3
$Z = 8$
$D_x = 2.541$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 69 reflections
$\theta = 6.04–14.91°$
$\mu = 4.88$ mm^{-1}
$T = 293$ K
Irregular
0.23 × 0.11 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
8569 measured reflections
990 independent reflections
805 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.022$
$\theta_{\rm max} = 24.9°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 333 min
intensity decay: 12.68%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.019$
$S = 1.026$
907 reflections
114 parameters
All H-atom parameters refined
Regina weighting scheme

$(\Delta/\sigma)_{\rm max} = 0.271$
$\Delta\rho_{\rm max} = 0.72$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.65$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

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

	x	y	z	$U_{\rm eq}$
Ga	0.21994 (4)	0.11349 (3)	0.56246 (3)	0.0126 (2)
F1	0.2204 (2)	0.2715 (2)	0.6314 (2)	0.0194 (8)
F2	0.0254 (2)	0.1042 (2)	0.6126 (2)	0.024 (1)
F3	0.2680 (2)	0.0361 (2)	0.7089 (2)	0.0210 (9)
F4	0.4191 (2)	0.1276 (2)	0.5343 (2)	0.024 (1)
F5	0.1765 (3)	0.1756 (2)	0.4123 (2)	0.029 (1)
O	0.2191 (3)	−0.0484 (2)	0.4845 (2)	0.023 (1)
N1	−0.0314 (4)	0.3097 (3)	0.7540 (3)	0.022 (1)
N2	−0.0315 (4)	0.4241 (3)	0.6892 (3)	0.022 (2)

Table 4. *Selected geometric parameters (Å, °) for (II)*

Ga—F1	1.894 (2)	Ga—F4	1.875 (2)
Ga—F2	1.887 (2)	Ga—F5	1.858 (2)
Ga—F3	1.899 (2)	Ga—O	1.975 (3)
F1—Ga—F2	85.98 (9)	F2—Ga—O	94.6 (1)
F1—Ga—F3	93.10 (8)	F3—Ga—F4	87.23 (9)
F1—Ga—F4	89.50 (9)	F3—Ga—F5	174.73 (9)
F1—Ga—F5	92.05 (9)	F3—Ga—O	89.0 (1)
F1—Ga—O	177.8 (1)	F4—Ga—F5	91.7 (1)
F2—Ga—F3	86.70 (9)	F4—Ga—O	90.2 (1)
F2—Ga—F4	172.22 (9)	F5—Ga—O	85.8 (1)
F2—Ga—F5	94.8 (1)		

For $(N_2H_5)_3[GaF_6]$ the maximum scan time was 60 s, the ω–2θ scan width was $(0.70 + 0.30\tan\theta)°$ and an orientation control was checked every 500 reflections; for $(N_2H_6)[GaF_5(H_2O)]$ the maximum scan time was 80 s, the ω–2θ scan width was $(0.90 + 0.30\tan\theta)°$ and an orientation control was checked every 300 reflections. For both compounds the background was measured as 1/4 of the scan on each side of the reflections and an aperture of $(2.4 + 0.9\tan\theta)°$ was used. The sizes of the crystals were such that no absorption corrections were necessary. Both structures were solved by the Patterson method and subsequent use of Fourier maps. The structures were then refined by full-matrix least-squares procedures using anisotropic displacement parameters for non-H atoms and isotropic for H atoms. Refinement of the positional and displacement parameters of the H atoms was stable; however, the final shift/e.s.d. for these parameters remained quite high. In the final stages of the refinement, the Regina weighting scheme (Wang Hong & Robertson, 1985) was used.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *X-ray PARAM* (local program); data reduction: *Xtal*3.2 *DIFDAT SORTRF ADDREF* (Hall, Flack & Stewart, 1992); program(s) used to solve structures: *Xtal*3.2; program(s) used to refine structures: *Xtal*3.2 *CRYLSQ*; molecular graphics: *ORTEP* (Johnson, 1965) and *ATOMS* (Dowty, 1991); software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

The financial support of the Ministry for Science and Technology of the Republic of Slovenia is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1142). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bukovec, P. & Golič, L. (1976). *Acta Cryst.* B**32**, 948–950.

Conant, J. W. & Roof, R. B. Jr (1970). *Acta Cryst.* B**26**, 1928–1932.

Dowty, E. (1991). *ATOMS. A Computer Program for Displaying Atomic Structures.* Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663. USA.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Frlec, B., Gantar, D., Golič, L. & Leban, I. (1984). *J. Fluorine Chem.* **25**, 271–279.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual.* Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Meden, A., Golič, L. & Šiftar, J. (1992). *Vestn. Slov. Kem. Drus.* **39**, 319–324.
Šiftar, J. & Bukovec, P. (1970). *Monatsh. Chem.* **101**, 1184–1188.
Wang Hong & Robertson, B. E. (1985). In *Structure and Statistics in Crystallography*, edited by A. J. C. Wilson. New York: Adenine Press.

Acta Cryst. (1996). C**52**, 496–497

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

Rebecca Berrigan and Bryan M. Gatehouse

Chemistry Department, Monash University, Clayton, Victoria, Australia 3168. E-mail: bryan.gatehouse@sci.monash.edu.au

(*Received 19 May 1995; accepted 10 October 1995*)

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.

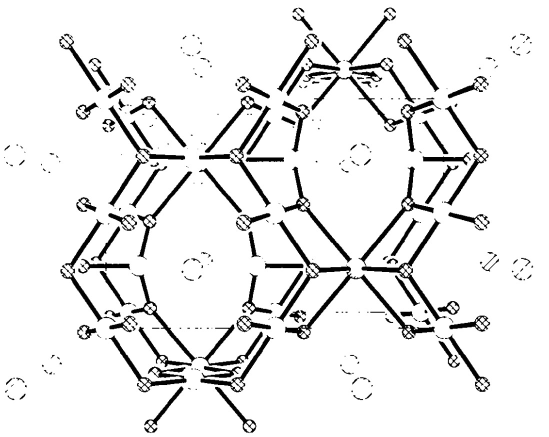

Fig. 1. *SHELXTL-Plus* (Sheldrick, 1991) diagram of $Cu_3Er(SeO_3)_2O_2Cl$ viewed along [001]. Striped spheres represent Cl atoms and cross-hatched spheres O atoms.

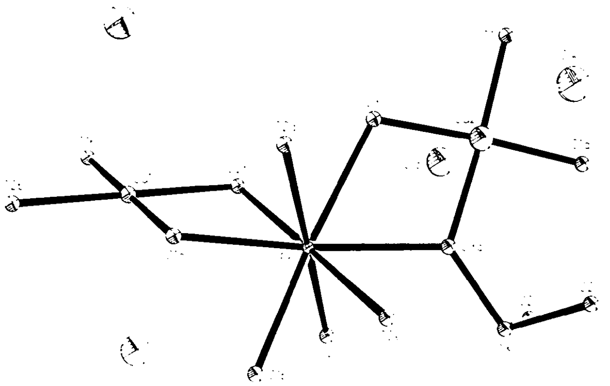

Fig. 2. *SHELXTL-Plus* (Sheldrick, 1991) diagram showing the O and Cl coordination of the Er, Cu1, Cu2 and Se ions. Lower case letters in atom numbers correspond to the symmetry transformations indicated here: (*a*) $x, y, z-1$; (*b*) $x, \frac{1}{2}-y, z-1$; (*c*) $-x, 1-y, 1-z$; (*d*) $\frac{1}{2}+x,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

---

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

Acta Crystallographica Section C
ISSN 0108-2701 ©1996