

## AN X-RAY CRYSTALLOGRAPHIC STUDY ON THE GEOMETRY OF THE STRUCTURE OF NONAAQUAEUROPIUM (III) TRIS (TRIFLUOROMETHANESULPHONATE)

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Crystals of the title compound are hexagonal,  $a=b=13.722(5)$  Å,  $c=7.504(2)$  Å, with two molecules per unit cell. Systematic absences are consistent with space group  $P6_3/m$ . The structure was solved by the heavy-atom method and was refined to a final residual index,  $R=0.059$  for 3139 unique reflections. The molecule consists of a cation  $[Eu(H_2O)_9]^{3+}$  and an anion  $[(CF_3SO_3)_3]^{3-}$  connected by hydrogen bonds. The metal atom is coplanar with three water oxygen atoms which are called the capping or equatorial oxygens. Another two sets each consisting of three oxygen atoms are lying in a plane symmetrically above and below the equatorial plane. A tricapped trigonal prism of nine water oxygen atoms surrounds the nine-coordinated Eu ion.

### INTRODUCTION

The crystal structures of some nona-aqualanthanide ethyl sulphates were first studied by Ketelaar [1] and later by Fitzwater and Rundle [2]. The symmetry of the crystal field at the metal site due to the nine coordinated oxygen atoms alone was postulated as being trigonal-dipyramidal. The structures of nona-aquaneodymium bromate and that of nona-aquasamarium bromate were determined by Helmholtz (from two-dimensional X-ray data) [3] and Sikka (from neutron diffraction data) [4] respectively. Both structures belong to the higher symmetry hexagonal space group  $C6mc$ . As with ethyl sulphates, the coordination polyhedra of the bromate structures are tricapped trigonal prisms with the oxygen atoms of the nine water molecules at the corners. The  $Nd^{3+}$  or  $Sm^{3+}$  ion is at the centre of the polyhedron. The orientations of the coordinated water molecules are different in the bromate and ethyl sulphate structures.

In view of these differences in the geometry of the structures, the complex cations containing a rare earth element with alternative anions are of interest. In this paper, structure determination and details of the geometry of the structure of the title compound will be described.

### EXPERIMENTAL

An approximately hexagonal prismatic crystal was mounted on an automatic four-circle Syntex P1 diffractometer equipped with a graphite monochromator to reflect  $MoK\alpha$  radiation ( $\lambda=0.71069$  Å). Unit cell parameters were obtained by a least-squares fit of 12 reflections with

$2\theta$  values ranging between  $20^\circ$  to  $30^\circ$ . Systematic absences in the intensity data (intensities are zero for  $00\ell$  reflection, where  $\ell=2n+1$ ) are consistent with the space group  $P6_3/m$ .

The intensity data were measured by a  $\theta - 2\theta$  step scan procedure. Measurements were made for each of 7533 reflections with  $2\theta \leq 85.5^\circ$  for various  $h, k, \ell$ . Crystal alignment and instrument stability was monitored by remeasuring six standard reflections (600, 600, 060, 060, 660, 660) after every 100 reflections which exhibited no significant intensity changes.

### REFINEMENT OF THE STRUCTURE

The symmetry-related reflections were averaged and were converted into a unique set of 3139 reflections. The intensities (1) were assigned variances  $\sigma^2(I)$  based on counting statistics. The intensities were converted to structure amplitudes by using the data reduction program DATRDN (XRAY 76 programme system) [5]. Corrections for Lorentz and polarization effects were calculated with the same programme. The absorption corrections\* were evaluated applying the analytical method of de Meulenaer and Tompa [6] using the programme ABSCOR (XRAY 76 programme system) [5].

The structure was solved by the heavy-atom method. A three-dimensional Patterson function revealed the position of the heavy atom Eu. The coordinates of the Eu atom were used to phase a three-dimensional electron density function in which all non-hydrogen atoms were easily recognized. A difference Fourier synthesis then made it

\*Linear absorption coefficient,  $\mu(Mo K\alpha) = 29.2 \text{ cm}^{-1}$ .

possible to locate the positions of all hydrogen atoms. The refinement of the trial structure was carried out with the full-matrix least squares programme CRYLSQ (XRAY 76 programme system) [5]. The refinement was first performed with individual isotropic temperature factors assigned to all atoms. In a following step, anisotropic temperature factors were assigned to all non-hydrogen atoms. The quantity minimized was  $D = \sum_j W_j (|F_{Oj}| - k|F_{Cj}|)^2$ , where  $k$  is the scale factor,  $w_j$  is the weight assigned to the  $j$ th observation and is equal to  $1/\sigma^2(F_{Oj})$ .

$F_{Oj}$  and  $F_{Cj}$  are the  $j$ th observed and calculated structure factors respectively. Least-squares refinement continued until all parameter shifts were  $0.1\sigma$  ( $\sigma$  denotes the estimated standard deviation of the parameter). The final residual index,  $R = (\sum_j |F_{Oj}| - |F_{Cj}|) / \sum_j |F_{Oj}|$ , converged to 0.059. The atomic scattering factors for all atoms were taken from International Tables for X-ray Crystallography [7] and the dispersion correction factors for all atoms were from Cromer and Liberman [8]. The X-ray structure factors for the title compound have been archived on a magnetic

Table 1. Some typical portion of the observed and calculated structure factors for the title compound.

h k l	$10F_o$	$10F_c$	h k l	$10F_o$	$10F_c$	h k l	$10F_o$	$10F_c$
0 1 0	600	-581	4 1 1	93	-104	2 2 2	968	-965
1 1 0	720	721	5 1 1	1023	1012	3 2 2	435	439
2 1 0	164	-156	0 2 1	1432	1359	4 2 2	745	750
3 1 0	517	-501	1 2 1	609	-594	0 3 2	978	-999
4 1 0	1051	1059	2 2 1	161	-155	1 3 2	121	119
5 1 0	97	106	3 2 1	1138	1145	2 3 2	789	745
0 2 0	797	-789	4 2 1	1206	-1204	3 3 2	1122	-1101
1 2 0	1397	-1359	5 2 1	33	36	4 3 2	602	592
2 2 0	86	78	0 3 1	250	-261	0 4 2	636	633
3 2 0	564	-597	1 3 1	1137	1084	1 4 2	1568	-1520
4 2 0	136	136	2 3 1	518	-509	2 4 2	94	82
5 2 0	933	941	3 3 1	45	38	3 4 2	529	515
0 3 0	1175	1167	4 3 1	322	324	4 4 2	926	-937
1 3 0	1183	-1144	5 3 1	440	-430	0 1 3	633	629
2 3 0	1039	1001	0 4 1	147	-133	1 1 3	29	16
3 3 0	968	938	1 4 1	247	243	2 1 3	1168	-1111
4 3 0	766	-765	2 4 1	101	114	3 1 3	956	933
5 3 0	105	-114	3 4 1	414	-413	4 1 3	308	300
0 4 0	693	-712	4 4 1	270	273	0 2 3	744	-719
1 4 0	958	929	5 4 1	672	683	1 2 3	735	760
2 4 0	763	-733	0 5 1	1221	1247	2 2 3	320	333
3 4 0	432	-422	1 5 5	1502	-1483	3 2 3	1023	-992
4 4 0	512	513	2 5 1	78	90	4 2 3	498	503
5 4 0	39	47	3 5 1	723	714	0 0 4	1772	1798
0 5 0	182	173	4 5 1	765	-758	0 1 4	677	-698
1 5 0	883	-850	5 5 1	284	282	1 1 4	807	799
2 5 0	615	603	0 0 2	1843	-1862	2 1 4	63	48
3 5 0	502	-496	0 1 2	206	208	3 1 4	103	-121
4 5 0	424	-428	1 1 2	439	-403	0 1 5	612	-633
5 5 0	574	580	2 1 2	470	-444	1 1 5	456	452
0 1 1	953	-935	3 1 2	945	922	2 1 5	597	589
1 1 1	1342	1289	4 1 2	950	-951	3 1 5	390	-372
2 1 1	1277	1278	0 2 2	722	697	0 0 6	1207	-1272
3 1 1	495	-490	1 2 2	1075	1025	0 1 6	257	274

\*Copies are available on application to the Director, Crystallography Centre, the University of Western Australia, WA 6009, Australia.

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and anisotropic thermal parameters,  $U_{ij}$ , ( $\text{\AA}^2 \times 10^4$ ) for different atoms of the title compound. E.s.d.'s in parentheses refer to the last significant digits.

Atoms	x/a	y/b	z/c	$U_{11}$ (or $U^+$ )	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Eu	6667*	3333*	2500*	276(1)	276(1)	264(1)	138(1)	0	0
O(1)	4892(2)	1420(2)	2500*	382(10)	415(11)	422(11)	68(9)	0	0
O(2)	6647(1)	2090(1)	218(2)	465(8)	319(7)	437(8)	158(6)	120(6)	-9(1)
O(3)	176(1)	6201(1)	883(2)	409(7)	690(10)	435(8)	160(7)	-38(7)	-160(8)
O(4)	1349(2)	7488(2)	2500*	291(9)	735(15)	442(12)	112(10)	0	0
H(1)	4501(19)	1036(20)	1532(35)	603(74)					
H(2a)	6422(23)	1526(24)	478(37)	605(90)					
H(2b)	7061(25)	2255(27)	-543(43)	922(120)					
S(1)	639(1)	6818(1)	2500*	294(3)	472(4)	325(3)	135(3)	0	0
C(1)	168(4)	7849(4)	2500*	729(27)	707(26)	832(30)	398(23)	0	0
F(1)	-941(2)	7328(3)	2500*	748(17)	1372(27)	1330(25)	744(19)	0	0
F(2)	538(2)	8474(2)	1080(3)	1555(21)	1152(17)	1417(19)	820(16)	251(17)	655(16)

\*Parameters constrained by symmetry. + Isotropic thermal parameters, U, for hydrogen atoms.

Table 3. Bond lengths and angles with the estimated standard deviations. The superscripts (i) – (ix) refer to the following equivalent sites of different atoms in the crystal structure.

- i)  $1+y-x, 1-x, z$  ii)  $1-y, x-y, z$  iii)  $x, y, \frac{1}{2}-z$  iv)  $1-y, x-y, \frac{1}{2}-z$  v)  $1+y-x, 1-x, \frac{1}{2}-z$  vi)  $y-x, -x, z$   
vii)  $1-x, 1-y, -z$  viii)  $1-(y-x), x, -z$  ix)  $y, y-x, -z$ .

Bond lengths in  $\text{\AA}$ 

Bond angles in deg.

## (a) Coordination Polyhedron:

Eu – O(1) = 2.536(2)

Eu – O(2) = 2.408(2)

O(2) – O(2<sup>iii</sup>) = 3.424 (3)

O(1) – Eu – O(2) = 66.5(1)

O(2) – Eu – O(2<sup>iii</sup>) = 90.7(1)

## (b) Water molecules:

O(1) – H(1) = 0.900(24)

O(2) – H(2a) = 0.702(30)

O(2) – H(2b) = 0.756(32)

H(1) – O(1) – H(1<sup>iii</sup>) = 107.6(20)

H(2a) – O(2) – H(2b) = 112.9(40)

## (c) Hydrogen bond system:

O(1) ... O(3<sup>viii</sup>) = 2.965(2)

O(2) ... O(3<sup>vi</sup>) = 2.827(3)

O(2) ... O(4<sup>vii</sup>) = 2.750(2)

O(1) – H(1) ... O(3<sup>viii</sup>) = 165.8(7)

O(2) – H(2a) ... O(3<sup>vi</sup>) = 167.0(5)

O(2) – H(2b) ... O(4<sup>vii</sup>) = 172.9(8)

tape following the standard crystallographic file structure recommended by the IUCr Data and Computing Commissions\*. Some typical portion of the observed and calculated structure factors are given in Table 1.

## RESULTS AND DISCUSSION

Atomic coordinates and temperature factors are listed in Table 2 and selected interatomic distances and angles in

Table 3. A projection of the unit cell contents and the cation – anion hydrogen bonding interactions viewed down the crystallographic *c*-axis is shown in Fig. 1.

The special position occupied by the europium atom is at  $(2/3, 1/3, 1/4)$ . The structure is composed of columns of cations,  $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$ , about  $\bar{6}$  axes and by the anions,  $[(\text{CF}_3\text{SO}_3)_3]^{3-}$ , about the  $6_3$  – axis through the origin. These columns of cations and anions in the crystal structure are linked by an extensive three dimensional network of hydrogen bonds. The coordination polyhedron of the cation,  $[\text{Eu}(\text{H}_2\text{O})_9]^{3+}$ , is a tricapped trigonal prism. All nine water molecules are coordinated about the europium ion; six at the corners of a trigonal prism at a distance  $2.408 \text{ \AA}$  and three out from the prism faces at a distance  $2.536 \text{ \AA}$  from the nine-coordinated Eu ion. Equatorial water molecules consists of O(1), H(1) and H(1<sup>iii</sup>) atoms. Two other equatorial water molecules may be located from symmetry transformations (Table 3). H(1) and H(1<sup>iii</sup>) are lying symmetrically above and below the equatorial plane. The Eu atom and three equatorial water oxygen atoms O(1), O(1<sup>i</sup>) and O(1<sup>ii</sup>) are situated at the equatorial (or mirror) plane,  $z/c = 1/4$ . The prism water molecule consists of O(2), H(2a) and H(2b) atoms. Other five prism oxygen atoms O(2<sup>i</sup>), O(2<sup>ii</sup>), O(2<sup>iii</sup>), O(2<sup>iv</sup>) and O(2<sup>v</sup>) are symmetrically related to O(2). Distance between the prism oxygen atoms, O(2) & O(2<sup>iii</sup>) lying symmetrically above and below the mirror plane is  $3.424(3) \text{ \AA}$  (Table 3). It is also evident from the same Table that the prismatic bond, Eu – O(2) is  $0.128 \text{ \AA}$  shorter than the equatorial Eu – O(1) bond. This difference in metal-water oxygen bond length for prism

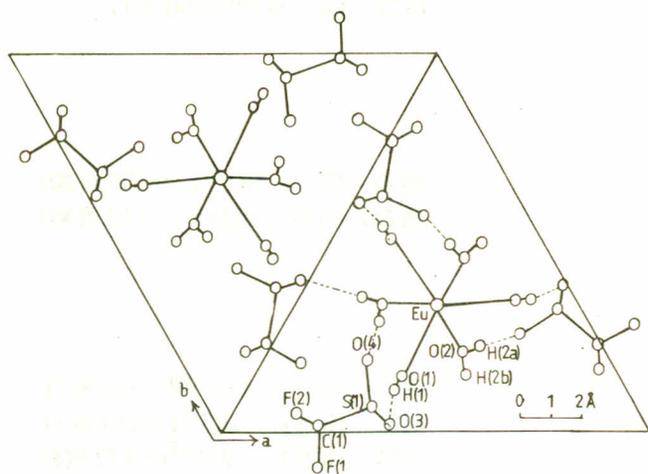


Figure 1. Projection of the unit cell contents and the cation – anion hydrogen bonding interactions viewed down the crystallographic *c*-axis.

and equatorial oxygen is probably caused by the repulsion between O(1) and O(2) atoms.

The anion,  $[(\text{CF}_3\text{SO}_3)_3]^{3-}$ , contains C(1), F(1), F(2), F(2<sup>iii</sup>), S(1), O(3), O(3<sup>iii</sup>) and O(4) atoms. O(3<sup>iii</sup>) and F(2<sup>iii</sup>) are symmetrically related to O(3) and F(2) atoms. When the spatial arrangement of atoms are projected onto a plane, O(3), O(3<sup>iii</sup>) and F(2) & F(2<sup>iii</sup>) merge to O(3) and F(2) respectively. The equatorial water oxygen O(1) is linked to O(3) atoms in the sulphonate group while the prism oxygen O(2) is linked to O(3) and O(4) sulphonate oxygens in another anion. The hydrogen atoms H(1), belonging to the equatorial water donate hydrogen bonds to the O(3) atoms of the sulphonate group. H(2a) and H(2b) belonging to the prism water donate bonds to O(3) and O(4) of another anion. Thus the sulphonate oxygen atoms are acceptors of the hydrogen bonds.

The hydrogen bond lengths vary between 2.75 and  $2.97 \text{ \AA}$ . O(2) . . . O(3<sup>vi</sup>) bonds are about  $0.14 \text{ \AA}$  shorter than O(1) . . . O(3<sup>viii</sup>) bond. Thus the former bond is stronger than that of latter. The O – H . . . O angles vary between  $165$  and  $173^\circ$  (Table 3). These hydrogen bond lengths and angles are close to those reported by Albertsson and Elding [9] for praseodymium and ytterbium ethyl sulphates.

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## REFERENCES

1. J. A. A. Ketelaar, *Physica*, **619** (1937).
2. D. R. Fitzwater and R. E. Rundle, *Z. Kristallogr.*, **112**, 362 (1959).
3. L. Helmholz, *J. Amer. Chem. Soc.*, **61**, 1544 (1939).
4. S. K. Sikka, *Acta Cryst.*, **A25**, 621 (1969).
5. The XRAY 76 program system (Tech. Report TR – 446), edited by J.M. Stewart, 1976, Computer Science Center, University of Maryland, College Park, USA.
6. J de Meulenaer and H. Tompa, *Acta Cryst.*, **19**, 1040 (1965).
7. *International Tables for X-ray Crystallography*, Vol. IV (eds.) J. A. Ibers and W. Hamilton, Birmingham: Kynoch Press, 1974).
8. D.T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
9. J. Albertsson and I. Elding, *Acta Cryst.*, **B33**, 1460 (1977).