Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dieuropium(III) silicodimonophosphatediphosphate

Jamal Bennazha,[a,b] Ali Boukhari[b] and Elizabeth M. Holt[c]*

[a]Département de Chimie, Faculté des Sciences et Techniques, Université Hassan-II, Mohammedia, Morocco, [b]Laboratoire de Chimie du Solide Appliquée, Laboratoire Associé Francophone, Département de Chimie, Faculté des Sciences, Université Mohammed-V, Avenue Ibn-Batouta, Rabat, Morocco, and [c]Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA

Correspondence e-mail:
betsy@biochem.okstate.edu

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Si–O) = 0.006 Å
Disorder in main residue
R factor = 0.025
wR factor = 0.064
Data-to-parameter ratio = 12.8

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

Received 18 February 2000
Accepted 18 January 2001
Online 30 January 2001

A new europium(III) silicophosphate, whose formula may be considered to be $Eu_2Si(PO_4)_2(P_2O_7)$, has been found to consist of phosphosilicate chains with Si—O—P—O—P—O—Si backbones extending in the *a* direction. The P_2O_7 group and the Si atom both lie on crystallographic twofold axes. Tetrahedral silicon is further bound to two monophosphate groups. This is a silicophosphate of previously unseen type.

Comment

The structural literature contains reports of only three silicophosphate materials with +3 charged cations. These contain two distinctly different silicophosphate moieties.

$RuSiP_3O_{11}$ (Fukuoka *et al.*, 1996) may be seen to exist with Si_2O_7 groups sharing each of its six terminal O atoms with a different P_2O_7 group. Each P_2O_7 group is seen to share a single O atom per PO_4 tetrahedron with an Si_2O_7 group, creating a three-dimensional network of linked tetrahedra which encapsulate Ru^{3+} cations. $MoSiP_3O_{11}$ (Leclaire & Raveau, 1987) shows the same motif, with Mo^{3+} encapsulated within the three-dimensional network of silicophosphates.

$Mo_3SiP_5O_{19}$ (Wang *et al.*, 1988) exists with isolated $(PO_3O)_3SiOSi(OPO_3)_3$ and $(PO_3O)_3POP(OPO_3)_3$ units stacked in columns parallel to the hexagonal *c* axis. $V_3SiP_5O_{19}$ (Leclaire *et al.*, 1986) appears to be isostructural with the molybedenum-containing compound of similar formula. $Mo_4Si_2P_6O_{25}$ (Leclaire *et al.*, 1988) shows a similar motif but with $(PO_3O)_3SiOSi(OPO_3)_3$ groups only.

$Eu_2Si(PO_4)_2(P_2O_7)$ crystallizes with silicophosphate chains with Si—O—P—O—P—O backbones extending in the *a* direction (Fig. 1). Tetrahedral silicon is further bound to two monophosphate groups, whereas the P atoms of the polymeric chain are further bonded to two terminal O atoms, O21 and O23 (Fig. 1). Thus, it is a silicophosphate of a previously unseen type.

Atoms O21, O22 and O23 display a 0.46/0.54 disorder with positions O21′, O22′ and O23′, and are related to them by a 23.3° rotation about the P2—O24 bond. Atoms O22 and O22′ lie on a twofold axis.

Eu atoms are localized between PO_3 groups and the two terminal O atoms of a P atom of the polymeric chain. Eu is within bonding distance of each of the disordered positions, O21, O21′, O23 and O23′. Eu^{3+} is six coordinate [average Eu—O 2.317 (6) Å], with a seventh Eu—O distance of 2.544 (5) Å. With the inclusion of the seventh distance, the geometry at europium appears to be that of a pentagonal bipyramid. Using bond-valence calculations to ascertain the validity of the

DOI: 101107/S1600536801001519

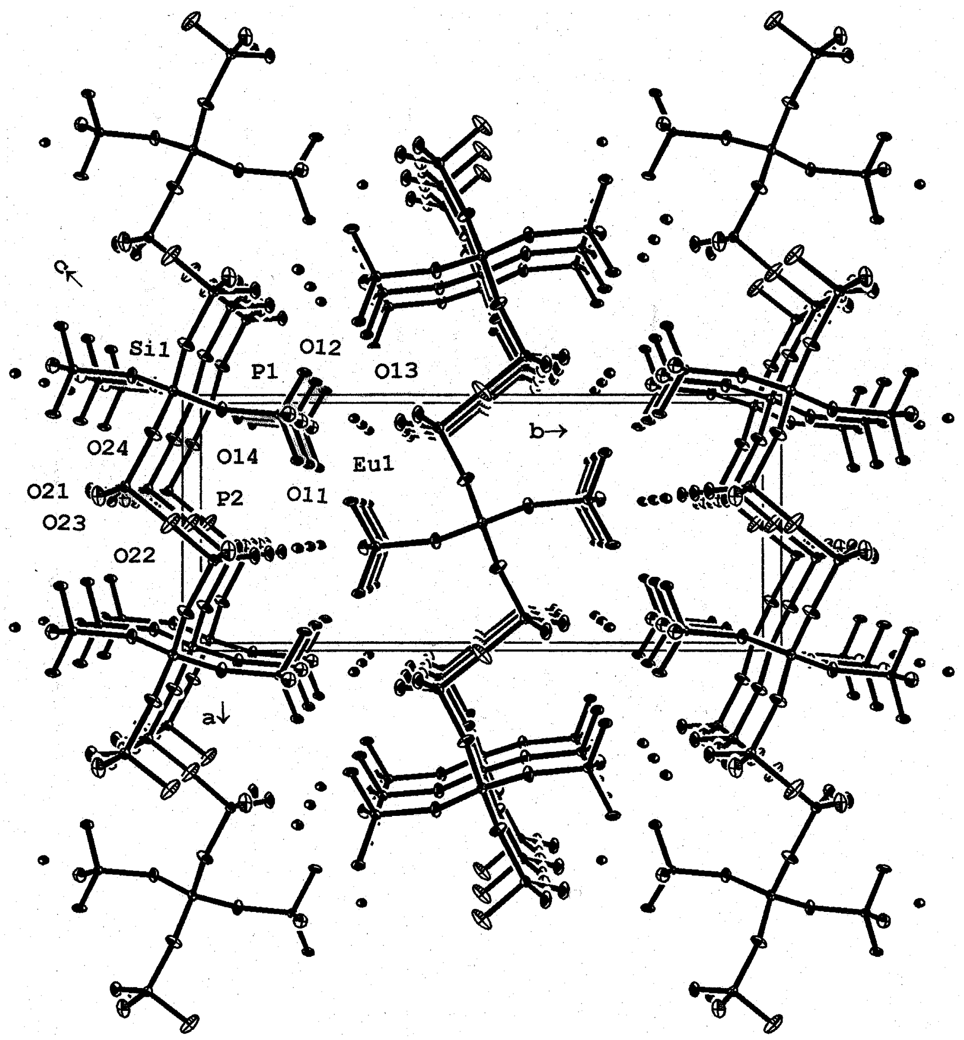

Figure 1
View of dieuropium(III) silicodimonophosphatediphosphate projected on the *ab* plane. Displacement ellipsoids are shown at the 50% probability level.

seventh distance (Brown, 1981) leads to a valence bond total of 3.065 using the six Eu—O distances of less than 2.451 (5) Å, but a significantly larger total of 3.352 Å if the seventh distance is included. Both geometry and valence-bond calculations argue that this longer distance is meaningful.

Silicon displays tetrahedral geometry, with an average Si—O distance of 1.604 (6) Å. Phosphorus tetrahedra have average P—O distances of 1.511 (11) Å.

Experimental

Crystal data

$Eu_2Si(PO_4)_2(P_2O_7)$
$M_r = 695.90$
Orthorhombic, $P2_12_12$
$a = 7.056$ (1) Å
$b = 16.376$ (3) Å
$c = 5.585$ (1) Å
$V = 645.34$ (19) Å^3
$Z = 2$
$D_x = 3.581$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 5.6$–16.9°
$\mu = 10.30$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.15 × 0.12 × 0.10 mm

Data collection

Syntex *P*4 four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1990)
$T_{min} = 0.181$, $T_{max} = 0.357$
1578 measured reflections
1422 independent reflections
1388 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 30.0°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 23$
$l = -1 \rightarrow 7$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.07$
1422 reflections
111 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 1.2737P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.012$
$\Delta\rho_{max} = 0.01$ e Å^{-3}
$\Delta\rho_{min} = -0.02$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0030 (4)

Table 1
Selected geometric parameters (Å, °).

Eu1—O21^{i}	2.217 (18)	Si1—O13	1.615 (5)
Eu1—O21$'^{i}$	2.344 (13)	P1—O11	1.514 (5)
Eu1—O23^{ii}	2.309 (15)	P1—O12	1.523 (5)
Eu1—O23$'^{ii}$	2.240 (12)	P1—O13	1.577 (5)
Eu1—O14^{iii}	2.267 (5)	P1—O14	1.504 (5)
Eu1—O12^{iv}	2.349 (4)	P2—O21	1.476 (18)
Eu1—O11^{v}	2.360 (4)	P2—O21$'$	1.496 (15)
Eu1—O12	2.451 (5)	P2—O22	1.536 (5)
Eu1—O11	2.544 (5)	P2—O22$'$	1.547 (5)
Si1—O24	1.593 (6)	P2—O23	1.520 (14)
Si1—O24^{vi}	1.593 (6)	P2—O23$'$	1.436 (12)
Si1—O13^{vi}	1.615 (5)	P2—O24	1.568 (5)
O21^{i}—Eu1—O14^{iii}	82.2 (5)	O21$'^{i}$—Eu1—O11	149.4 (4)
O23$'^{ii}$—Eu1—O14^{iii}	169.9 (4)	O12—Eu1—O11	57.32 (14)
O21^{i}—Eu1—O23^{ii}	87.6 (5)	O24—Si1—O24^{vi}	103.6 (5)
O14^{iii}—Eu1—O23^{ii}	169.7 (4)	O24—Si1—O13^{vi}	112.5 (3)
O21^{i}—Eu1—O12^{iv}	78.4 (5)	O24^{vi}—Si1—O13^{vi}	111.4 (3)
O23$'^{ii}$—Eu1—O12^{iv}	82.1 (4)	O24—Si1—O13	111.4 (3)
O14^{iii}—Eu1—O12^{iv}	88.8 (2)	O24^{vi}—Si1—O13	112.5 (3)
O23^{ii}—Eu1—O12^{iv}	88.0 (5)	O13^{vi}—Si1—O13	105.6 (4)
O21^{i}—Eu1—O11^{v}	87.9 (5)	O14—P1—O11	115.4 (3)
O23$'^{ii}$—Eu1—O11^{v}	96.4 (4)	O14—P1—O12	114.6 (3)
O14^{iii}—Eu1—O11^{v}	93.5 (2)	O11—P1—O12	104.2 (3)
O23^{ii}—Eu1—O11^{v}	87.4 (5)	O14—P1—O13	107.8 (3)
O12^{iv}—Eu1—O11^{v}	165.72 (15)	O11—P1—O13	107.5 (3)
O14^{iii}—Eu1—O21$'^{i}$	95.7 (4)	O12—P1—O13	106.8 (3)
O12^{iv}—Eu1—O21$'^{i}$	83.9 (4)	O21—P2—O23	116.4 (8)
O11^{v}—Eu1—O21$'^{i}$	81.9 (4)	O21—P2—O22	108.9 (10)
O21^{i}—Eu1—O12	156.9 (5)	O23—P2—O22	108.8 (11)
O23$'^{ii}$—Eu1—O12	83.2 (4)	O21—P2—O24	110.7 (8)
O14^{iii}—Eu1—O12	98.71 (18)	O23—P2—O24	109.6 (8)
O23^{ii}—Eu1—O12	91.1 (4)	O22—P2—O24	101.5 (2)
O12^{iv}—Eu1—O12	124.68 (12)	O23$'$—P2—O22$'$	109.0 (9)
O11^{v}—Eu1—O12	68.94 (15)	O21$'$—P2—O22$'$	109.7 (9)
O21$'^{i}$—Eu1—O12	148.0 (4)	O23$'$—P2—O24	108.4 (6)
O21^{i}—Eu1—O11	145.8 (5)	O23$'$—P2—O21$'$	118.1 (7)
O23$'^{ii}$—Eu1—O11	78.3 (4)	O21$'$—P2—O24	108.4 (6)
O14^{iii}—Eu1—O11	94.34 (18)	O22$'$—P2—O24	102.2 (2)
O23^{ii}—Eu1—O11	93.4 (4)	P2^{vii}—O22—P2	158 (2)
O12^{iv}—Eu1—O11	67.52 (15)	P2—O22$'$—P2^{vii}	154.1 (16)
O11^{v}—Eu1—O11	126.26 (12)		

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

The orthorhombic cell displayed absences $h00$, $h = 2n$ and $0k0$, $k = 2n$, fixing the space group as $P2_12_12$. Disorder of three O atoms became apparent as refinement progressed. The P_2O_7 group exists with a twofold axis passing through the bridging O atom, which was seen to exist in two positions O22 and O22′, both on the twofold axis. While P2 and O24 were seen in ordered positions, alternate or disordered positions were seen for terminal O atoms O21 (O21′) and O23 (O23′). O21, O22, O23 and O24 form a tetrahedral array about P2 as do O21′, O22′ O23′ and O24. The disorder may be understood in terms of an approximately 22° rotation about the P2—O24 (and the P2*a*—O24*a* bond related by the twofold axis) corresponding to the bridging O atom being ‘up’ or ‘down’ and resulting in a 0.59 Å displacement of each of the disordered atoms. O21 and O23 were refined with an occupancy parameter equal to x (O22 occupancy = $0.5x$) whereas O21′ and O23′ were refined with an occupancy parameter of $1 - x$ [O22′ occupancy = $(1 - x)/2$]. The refined value of x is 0.46 (3). Anisotropic displacement parameters for pairs of close atoms (O21/O21′, O22/O22′ and O23/O23′) were constrained to identical values for each pair. The identity of the Si atom was confirmed by observing that the occupancy parameter refined to the correct value (0.5), confirming the electron density of the position, by comparing the Si—O distances with those of the literature and by observing the charge neutrality of the structure which requires a +4 cation in that position.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*97.

JB acknowledges the support of the Moroccan–American Commission in the form of a Fullbright grant which has made this research possible.

References

Brown, I. D. (1981). *Struct. Bonding Cryst.* **2**, 1–30.
Fukuoka, H., Imoto, H. & Sato, T. (1996). *J. Solid State Chem.* **121**, 247–250.
Leclaire, A., Chahboun, H., Groult, D. & Raveau, B. (1986). *J. Solid State Chem.* **65**, 168–177.
Leclaire, A., Lamire, M. & Raveau, B. (1988). *Acta Cryst.* C**44**, 1181–1184.
Leclaire, A. & Raveau, B. (1987). *J. Solid State Chem.* **71**, 283–290.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Siemens (1990). *XP*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1991). *XSCANS Users Manual*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
Wang, S. L., Wang, C. C. & Lii, K. H. (1988). *J. Solid State Chem.* **74**, 409–413.