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Dysprosium thiosilicate, $Dy_4(SiS_4)_3$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(S–Si) = 0.002 Å
R factor = 0.023
wR factor = 0.047
Data-to-parameter ratio = 24.2

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

$Dy_4(SiS_4)_3$ is isotypic with $Tb_4(SiS_4)_3$ [Hatscher & Urland (2002). *Z. Anorg. Allg. Chem.* **628**, 1673–1677]. It contains almost undistorted, isolated $(SiS_4)^{4-}$ tetrahedra and four crystallographically different Dy positions with coordination numbers seven and eight.

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Comment

Only a few thiosilicate compounds with lanthanide ions are known: Ln_2SiS_5 (Ln = La–Nd) with unknown structure (Michelet *et al.*, 1970), $Ln_6Si_{2.5}S_{14}$ (Ln = Gd–Dy, Y) (Michelet & Flahaut, 1969; Perez & Duale, 1969), trigonal $Ln_4Si_3S_{12}$ (Ln = Ce–Sm, Gd) (Perez & Duale, 1969), and more recently Eu_2SiS_4 (Johrendt & Pocha, 2001). In all the reported structures, isolated SiS_4 tetrahedra are a dominant feature, one exception being the second Si position in $Ln_6Si_{2.5}S_{14}$, which is coordinated by six sulfides in the shape of a slightly distorted octahedron. Also known are lanthanide thiogermanates, such as $La_4(GeS_4)_3$ (Mazurier & Etienne, 1974) containing isolated GeS_4 groups. The formation of corner-sharing tetrahedra resulting in $Si_2O_7^{6-}$ anions, commonly seen in lanthanide oxosilicates, is up to now unknown for the lanthanide thiosilicates.

We recently reported the structure of a new lanthanide thiosilicate $Tb_4(SiS_4)_3$ (Hatscher & Urland, 2002) and present here the homologous dysprosium compound. The isolated $(SiS_4)^{4-}$ tetrahedra (Fig. 1) are slightly distorted and contain Si—S distances between 2.062 (2) and 2.150 (2) Å, in agreement with those reported for SiS_2 (Buessem *et al.*, 1935). $La_4(GeS_4)_3$ has a similar formula but the arrangement of tetrahedra differs (Mazurier & Etienne, 1974). There is no known lanthanide oxosilicate analogue.

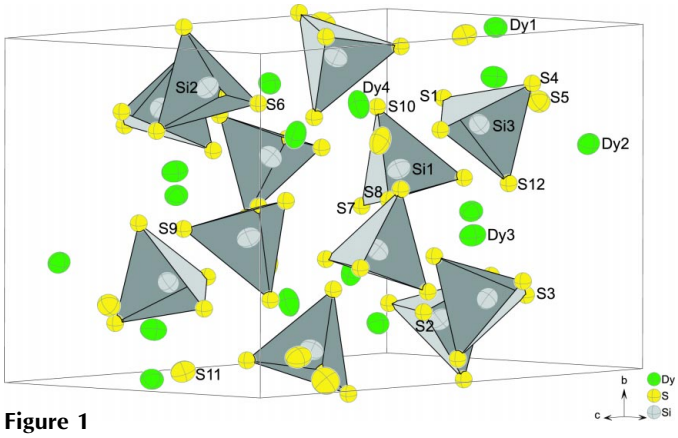

Figure 1
View of $Dy_4(SiS_4)_3$. The isolated SiS_4 building blocks are indicated by grey tetrahedra.

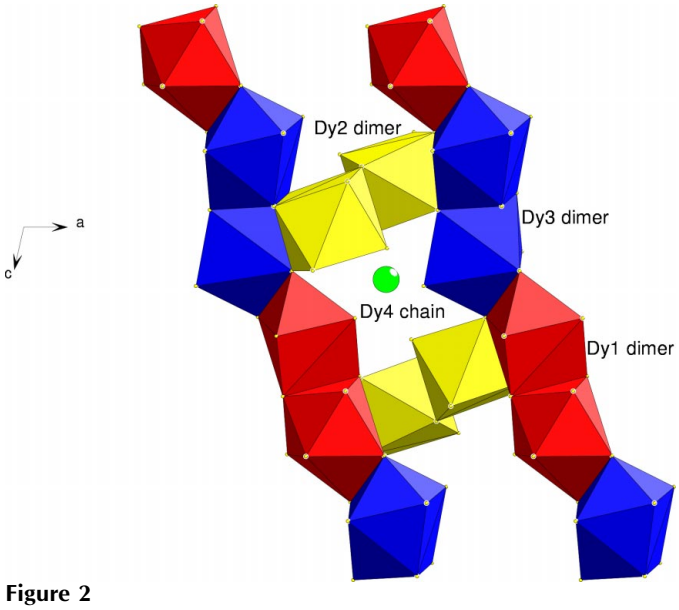

Figure 2
The connection theme of $Dy_4(SiS_4)_3$, viewed along the *b* axis. Dy1 polyhedra are in red, Dy2 in yellow and Dy3 in blue. In the centre, one Dy4 is depicted.

The Dy1, Dy2 and Dy3 ions are each coordinated by eight sulfide ions. Two $Dy1S_8$ polyhedra share edges to form dimers. The same basic motif can be found for Dy2 and Dy3. Dy4 is surrounded by only seven sulfide ions and forms infinite chains along [010] by sharing two opposite corners with other $Dy4S_7$ building blocks. The dimers of Dy1, Dy2, and Dy3 form a three-dimensional network consisting of alternating building blocks, which results in a channel structure that is filled by the one-dimensional chain of Dy4 (Fig. 2).

Experimental

Dysprosium metal chips (StremChem, 99.9%), sulfur powder (Aldrich, 99.98%), silicon powder (Merck, >99%), and bromine (Riedel-de Haën, >99%) were added in a quartz glass tube in a ratio of 1:3.28:1.06:∼0.3. The ampoule was evacuated, sealed, and heated for 10 d in a temperature gradient of 1273 to 1073 K. After the tube was cooled, a few air-stable, green crystals were obtained.

Crystal data

$Dy_4(SiS_4)_3$
M_r = 1118.99
Monoclinic, $P2_1/n$
a = 9.813 (2) Å
b = 10.9387 (18) Å
c = 16.360 (4) Å
β = 102.86 (3)°
V = 1712.1 (6) Å^3
Z = 4
D_x = 4.341 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7997 reflections
θ = 2.5–28.1°
μ = 18.91 mm^{-1}
T = 293 (2) K
Plate, green
0.22 × 0.10 × 0.02 mm

Data collection

Stoe IPDS diffractometer
1.2° φ scans
Absorption correction: Gaussian (*X-RED*; Stoe & Cie, 1998)
T_{min} = 0.117, T_{max} = 0.685
29 396 measured reflections
4184 independent reflections
3327 reflections with $I > 2\sigma(I)$
R_{int} = 0.120
θ_{max} = 28.2°
h = −12 → 13
k = −14 → 14
l = −21 → 21

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.047
S = 0.87
4184 reflections
173 parameters
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.29 e Å^{-3}
$\Delta\rho_{min}$ = −1.42 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00081 (4)

Table 1
Selected geometric parameters (Å).

Dy1—S11^{i}	2.7597 (15)	Dy3—S4^{viii}	2.9780 (16)
Dy1—S1	2.7740 (15)	Dy3—S9^{vi}	3.2680 (15)
Dy1—S11^{ii}	2.7962 (14)	Dy4—S1	2.6809 (14)
Dy1—S4	2.8194 (13)	Dy4—S2^{ix}	2.7629 (13)
Dy1—S3^{iii}	2.8338 (15)	Dy4—S6^{x}	2.7844 (16)
Dy1—S2^{iii}	2.9464 (14)	Dy4—S10	2.8263 (16)
Dy1—S5	3.0625 (15)	Dy4—S7^{ix}	2.8289 (15)
Dy1—S12^{iv}	3.1243 (16)	Dy4—S8^{ix}	2.9079 (16)
Dy2—S5	2.7924 (13)	Dy4—S8	3.2526 (17)
Dy2—S10^{v}	2.8114 (13)	Si1—S7	2.1504 (19)
Dy2—S7^{v}	2.8460 (15)	Si1—S8	2.128 (2)
Dy2—S12	2.8783 (15)	Si1—S9^{ii}	2.114 (2)
Dy2—S6^{vi}	2.8903 (16)	Si1—S10	2.083 (2)
Dy2—S9^{vi}	2.9512 (15)	Si2—S2^{ii}	2.138 (2)
Dy2—S4	2.9688 (15)	Si2—S5^{xi}	2.124 (2)
Dy2—S7^{vii}	2.9691 (16)	Si2—S6	2.0757 (17)
Dy3—S3	2.7580 (14)	Si2—S11^{iii}	2.062 (2)
Dy3—S9^{ii}	2.8281 (15)	Si3—S1	2.1003 (17)
Dy3—S12	2.8520 (13)	Si3—S3^{iv}	2.093 (2)
Dy3—S8	2.8774 (15)	Si3—S4	2.1458 (19)
Dy3—S5^{vii}	2.8809 (15)	Si3—S12	2.126 (2)
Dy3—S2	2.8921 (15)		

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

Data collection: *IPDS Software* (Stoe & Cie, 1998); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

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