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Zirconium(IV) dilanthanum(III) pentasulfide

Adam D. Raw and James A. Ibers*

Department of Chemistry, Northwestern University, 2145 Sheridan Rd, Evanston, IL 60208-3113, USA
Correspondence e-mail: ibers@chem.northwestern.edu

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(Zr–S) = 0.001 Å; R factor = 0.017; wR factor = 0.056; data-to-parameter ratio = 20.2.

Zirconium(IV) dilanthanum(III) pentasulfide, $ZrLa_2S_5$, crystallizes with four formula units in the space group *Pnma* in the U_3S_5 structure type. The asymmetric unit comprises one Zr, one La and four S atoms. The Zr and three S atoms are situated on mirror planes. The structure consists of LaS_8 face-sharing bicapped distorted trigonal prisms and ZrS_7 edge-sharing monocapped octahedra.

Related literature

The cell parameters of $ZrLa_2S_5$ were previously reported from X-ray powder diffraction measurements (Kokhno & Serebrennikov, 1977). In a separate study, single-crystal X-ray diffraction measurements were used to determine the lattice parameters but not the structural parameters (Donohue & Jeitschko, 1974). Given that these lattice parameters, the space group, and the stoichiometry are similar to those of U_3S_5, it was assumed that $ZrLa_2S_5$ and U_3S_5 are isotypic (Donohue & Jeitschko, 1974). For analogous structures, see: Du Pont de Nemours (1976) and Potel *et al.* (1972). Physical property measurements of this and related compounds have been reported. For optical properties, see: Alekseeva *et al.* (1980); for electrical properties, see: Senova *et al.* (1984). For synthetic details, see: Jin *et al.* (2009). For ionic radii, see: Shannon (1976). For standardization of structural data, see: Gelato & Parthé (1987).

Experimental

Crystal data

$ZrLa_2S_5$ M_r = 529.34
Orthorhombic, *Pnma*
a = 11.4784 (4) Å
b = 8.2010 (3) Å
c = 7.3799 (3) Å
V = 694.70 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 14.93 mm^{-1}
T = 100 K
0.12 × 0.11 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: numerical [face indexed (*SADABS*; Bruker, 2009)]
T_{min} = 0.263, T_{max} = 0.340
8134 measured reflections
890 independent reflections
877 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.056
S = 2.51
890 reflections
44 parameters
$\Delta\rho_{max}$ = 2.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2549).

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S1. Comment

Single crystals of $ZrLa_2S_5$ resulted from attempts to synthesize zirconium analogues of the uranium lanthanide oxysulfide compound $UYb_2O_2S_3$ (Jin *et al.*, 2009).

$ZrLa_2S_5$ adopts the U_3S_5 structure type (Potel *et al.*, 1972). The unit-cell dimensions have been previously reported from single-crystal X-ray diffraction data (Donohue & Jeitschko, 1974) and from powder X-ray diffraction data (Kokhno & Serebrennikov, 1977). Unit-cell dimensions for $ZrLa_2S_5$ from the two single-crystal determinations compare favorably: a = 11.4864 (5), b = 8.2167 (5), c = 7.3894 (3) Å at room temperature (Donohue & Jeitschko, 1974) *versus* a = 11.4784 (4), b = 8.2010 (3), c = 7.3799 (3) Å from the present study at 100 K. (See also Kokhno & Serebrennikov, 1977). Isostructural compounds have been previously reported based on X-ray powder diffraction measurements for all trivalent lanthanides and yttrium excluding promethium, europium and ytterbium (Du Pont de Nemours, 1976).

The La—S interatomic distances (Table 1, Fig. 1) in the face-sharing bicapped distorted trigonal prisms LaS_8 (Fig. 2) range from 2.8861 (8) to 3.0698 (9) Å. The Zr—S distances range from 2.5704 (8) to 2.7421 (11) Å. These values are close to the distances of 3.00 Å for La—S and 2.62 Å for Zr—S calculated from the summed ionic radii (Shannon, 1976).

Physical property measurements of $ZrLa_2S_5$ have been reported by Alekseeva *et al.* (1980) and Senova *et al.* (1984).

S2. Experimental

ZrO_2 (99.99%, Aldrich) and La_2S_3 (99.9%, Strem) were used as received. Sb_2S_3 was synthesized from the elements. $ZrLa_2S_5$ was crystallized in a two step reaction in carbon-coated fused-silica tubes that had been evacuated to 10^{-4} Torr. In the first step, 0.02 g (0.16 mmol) ZrO_2 and 0.3 g (0.08 mmol) La_2S_3 were heated at 1273 K for 99 h and cooled to 298 K in 14 h. The resulting powder was combined with 0.02 g (0.06 mmol) Sb_2S_3 and heated at 1273 K for 99 h then cooled to 873 K at a rate of 2 K/h before cooling to 298 K over 10 h. The resulting $ZrLa_2S_5$ formed black prismatic crystals in low yield (<5 wt%). These were mechanically separated from the remaining powder.

S3. Refinement

The atomic positions were standardized with use of the program *STRUCTURE TIDY* (Gelato & Parthé, 1987). The highest peak of 2.2 (2) e/Å^3 is 0.50 Å and the deepest hole of -0.5 (2) e/Å^3 is 0.99 Å from the Zr position.

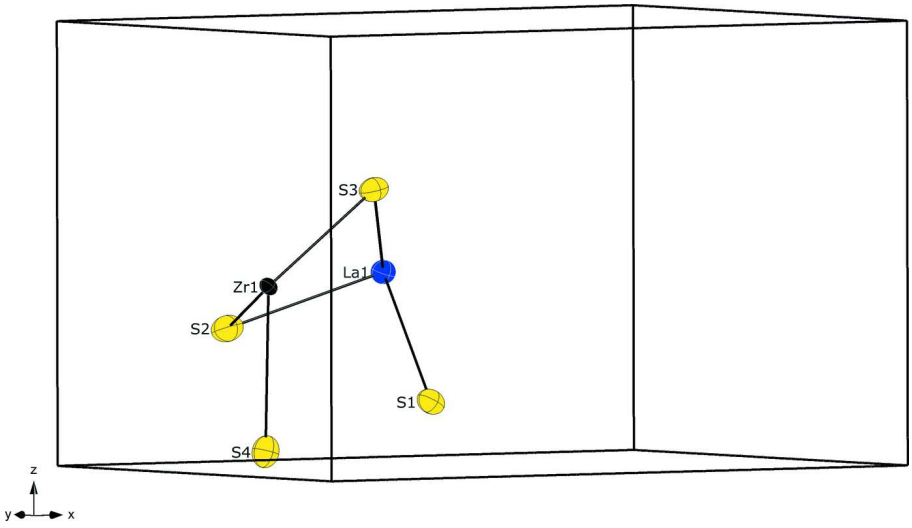

Figure 1

The asymmetric unit of $ZrLa_2S_5$. Displacement ellipsoids are displayed at the 95% probability level.

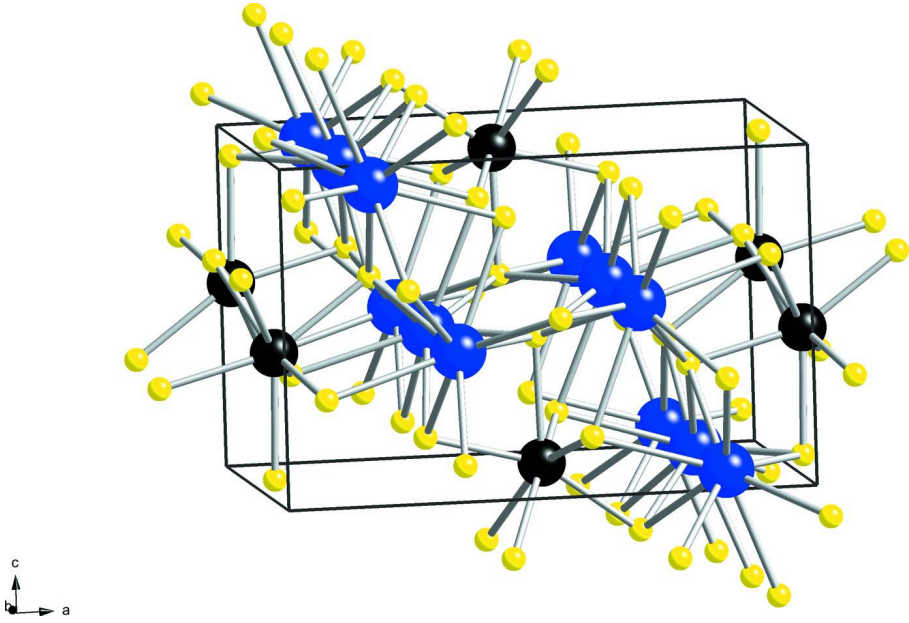

Figure 2

The $ZrLa_2S_5$ structure. La atoms are blue, Zr atoms are black, S atoms are yellow

Zirconium(IV) dilanthanum(III) pentasulfide

Crystal data

$ZrLa_2S_5$
M_r = 529.34
Orthorhombic, *Pnma*
a = 11.4784 (4) Å
b = 8.2010 (3) Å
c = 7.3799 (3) Å
V = 694.70 (5) Å^3
Z = 4
F(000) = 936
D_x = 5.061 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6255 reflections
θ = 3.1–27.9°
μ = 14.93 mm^{-1}

T = 100 K
Prism, black

0.12 × 0.11 × 0.09 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: numerical [face indexed (*SADABS*; Bruker, 2009)]
T_{min} = 0.263, T_{max} = 0.340

8134 measured reflections
890 independent reflections
877 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 27.9°, θ_{min} = 3.3°
h = −14→15
k = −10→6
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.056
S = 2.51
890 reflections
44 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
$[1.00000 + 0.00000\exp(0.00(\sin\theta/\lambda)^2)]/ [\sigma^2(F_o^2) + 0.0000 + 0.0000*P + (0.0158P)^2 + 0.0000\sin\theta/\lambda]$ where $P = 1.00000F_o^2 + 0.00000F_c^2$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0015 (2)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
La1	0.328759 (18)	0.501789 (17)	0.44160 (3)	0.00537 (12)
Zr1	0.01001 (3)	0.2500	0.42914 (5)	0.00286 (13)
S1	0.29147 (10)	0.2500	0.15995 (15)	0.0061 (2)
S2	0.07363 (7)	0.53474 (10)	0.32234 (11)	0.00812 (18)
S3	0.19311 (10)	0.2500	0.64058 (15)	0.0063 (2)
S4	0.00443 (9)	0.2500	0.05768 (14)	0.0073 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.00643 (17)	0.00439 (17)	0.00529 (17)	0.00023 (5)	−0.00022 (6)	−0.00036 (5)
Zr1	0.0030 (2)	0.0028 (2)	0.0028 (2)	0.000	−0.00063 (13)	0.000
S1	0.0073 (5)	0.0053 (5)	0.0056 (5)	0.000	−0.0013 (4)	0.000

S2	0.0102 (4)	0.0080 (3)	0.0062 (4)	0.0004 (3)	0.0007 (3)	−0.0005 (3)
S3	0.0086 (5)	0.0051 (5)	0.0051 (5)	0.000	0.0008 (4)	0.000
S4	0.0066 (6)	0.0062 (5)	0.0090 (6)	0.000	0.0007 (4)	0.000

Geometric parameters (Å, º)

La1—S4^{i}	2.8861 (8)	Zr1—S2^{viii}	2.7206 (9)
La1—S4^{ii}	2.9230 (7)	Zr1—S2^{ix}	2.7206 (9)
La1—S1^{ii}	2.9402 (8)	Zr1—S4	2.7421 (11)
La1—S1	2.9610 (8)	S1—Zr1^{i}	2.5932 (12)
La1—S3	2.9740 (8)	S1—La1^{x}	2.9402 (8)
La1—S3^{iii}	3.0235 (8)	S1—La1^{iii}	2.9402 (8)
La1—S2^{ii}	3.0398 (8)	S1—La1^{vi}	2.9609 (8)
La1—S2	3.0698 (9)	S2—Zr1^{viii}	2.7206 (9)
La1—La1^{iv}	4.0247 (4)	S2—La1^{iii}	3.0398 (8)
La1—La1^{v}	4.0712 (3)	S3—La1^{vi}	2.9739 (8)
La1—La1^{iii}	4.1092 (2)	S3—La1^{ii}	3.0235 (8)
La1—La1^{ii}	4.1092 (2)	S3—La1^{xi}	3.0235 (8)
Zr1—S2^{vi}	2.5704 (8)	S4—La1^{xii}	2.8861 (8)
Zr1—S2	2.5705 (8)	S4—La1^{vii}	2.8861 (8)
Zr1—S1^{vii}	2.5932 (12)	S4—La1^{iii}	2.9230 (7)
Zr1—S3	2.6176 (12)	S4—La1^{x}	2.9230 (7)
S4^{i}—La1—S4^{ii}	92.295 (9)	S2—La1—La1^{ii}	80.696 (17)
S4^{i}—La1—S1^{ii}	145.31 (3)	La1^{iv}—La1—La1^{ii}	103.733 (7)
S4^{ii}—La1—S1^{ii}	70.41 (3)	La1^{v}—La1—La1^{ii}	90.408 (4)
S4^{i}—La1—S1	66.63 (3)	La1^{iii}—La1—La1^{ii}	127.785 (11)
S4^{ii}—La1—S1	141.82 (3)	S2^{vi}—Zr1—S2	130.58 (4)
S1^{ii}—La1—S1	143.100 (13)	S2^{vi}—Zr1—S1^{vii}	101.36 (2)
S4^{i}—La1—S3	82.42 (2)	S2—Zr1—S1^{vii}	101.36 (2)
S4^{ii}—La1—S3	132.98 (3)	S2^{vi}—Zr1—S3	87.40 (2)
S1^{ii}—La1—S3	87.96 (2)	S2—Zr1—S3	87.40 (2)
S1—La1—S3	77.69 (2)	S1^{vii}—Zr1—S3	158.10 (3)
S4^{i}—La1—S3^{iii}	122.76 (3)	S2^{vi}—Zr1—S2^{viii}	153.69 (2)
S4^{ii}—La1—S3^{iii}	78.51 (2)	S2—Zr1—S2^{viii}	73.59 (3)
S1^{ii}—La1—S3^{iii}	84.12 (2)	S1^{vii}—Zr1—S2^{viii}	80.19 (3)
S1—La1—S3^{iii}	86.66 (2)	S3—Zr1—S2^{viii}	83.19 (3)
S3—La1—S3^{iii}	141.885 (17)	S2^{vi}—Zr1—S2^{ix}	73.59 (3)
S4^{i}—La1—S2^{ii}	70.75 (3)	S2—Zr1—S2^{ix}	153.69 (2)
S4^{ii}—La1—S2^{ii}	63.66 (2)	S1^{vii}—Zr1—S2^{ix}	80.19 (3)
S1^{ii}—La1—S2^{ii}	74.61 (3)	S3—Zr1—S2^{ix}	83.19 (3)
S1—La1—S2^{ii}	129.30 (2)	S2^{viii}—Zr1—S2^{ix}	80.92 (4)
S3—La1—S2^{ii}	70.62 (3)	S2^{vi}—Zr1—S4	72.55 (2)
S3^{iii}—La1—S2^{ii}	140.91 (2)	S2—Zr1—S4	72.55 (2)
S4^{i}—La1—S2	136.89 (2)	S1^{vii}—Zr1—S4	73.97 (3)
S4^{ii}—La1—S2	130.36 (2)	S3—Zr1—S4	127.93 (4)
S1^{ii}—La1—S2	69.42 (3)	S2^{viii}—Zr1—S4	131.74 (2)
S1—La1—S2	73.87 (3)	S2^{ix}—Zr1—S4	131.74 (2)

S3—La1—S2	72.74 (3)	Zr1^{i}—S1—La1^{x}	108.37 (3)
S3^{iii}—La1—S2	69.57 (3)	Zr1^{i}—S1—La1^{iii}	108.37 (3)
S2^{ii}—La1—S2	128.71 (2)	La1^{x}—S1—La1^{iii}	87.63 (3)
S4^{i}—La1—La1^{iv}	46.526 (16)	Zr1^{i}—S1—La1^{vi}	92.19 (3)
S4^{ii}—La1—La1^{iv}	45.769 (15)	La1^{x}—S1—La1^{vi}	88.267 (9)
S1^{ii}—La1—La1^{iv}	110.25 (2)	La1^{iii}—S1—La1^{vi}	159.29 (4)
S1—La1—La1^{iv}	106.65 (2)	Zr1^{i}—S1—La1	92.19 (3)
S3—La1—La1^{iv}	113.61 (2)	La1^{x}—S1—La1	159.29 (4)
S3^{iii}—La1—La1^{iv}	104.09 (2)	La1^{iii}—S1—La1	88.267 (9)
S2^{ii}—La1—La1^{iv}	56.031 (16)	La1^{vi}—S1—La1	88.43 (3)
S2—La1—La1^{iv}	173.643 (17)	Zr1—S2—Zr1^{viii}	106.41 (3)
S4^{i}—La1—La1^{v}	135.682 (15)	Zr1—S2—La1^{iii}	107.38 (3)
S4^{ii}—La1—La1^{v}	45.861 (14)	Zr1^{viii}—S2—La1^{iii}	144.80 (3)
S1^{ii}—La1—La1^{v}	46.186 (15)	Zr1—S2—La1	95.92 (3)
S1—La1—La1^{v}	134.217 (15)	Zr1^{viii}—S2—La1	101.56 (3)
S3—La1—La1^{v}	133.973 (16)	La1^{iii}—S2—La1	84.53 (2)
S3^{iii}—La1—La1^{v}	47.682 (15)	Zr1—S3—La1^{vi}	97.24 (3)
S2^{ii}—La1—La1^{v}	95.655 (16)	Zr1—S3—La1	97.24 (3)
S2—La1—La1^{v}	84.950 (15)	La1^{vi}—S3—La1	87.95 (3)
La1^{iv}—La1—La1^{v}	90.417 (4)	Zr1—S3—La1^{ii}	111.80 (3)
S4^{i}—La1—La1^{iii}	107.70 (2)	La1^{vi}—S3—La1^{ii}	150.89 (4)
S4^{ii}—La1—La1^{iii}	123.806 (19)	La1—S3—La1^{ii}	86.491 (11)
S1^{ii}—La1—La1^{iii}	106.89 (2)	Zr1—S3—La1^{xi}	111.80 (3)
S1—La1—La1^{iii}	45.659 (16)	La1^{vi}—S3—La1^{xi}	86.491 (11)
S3—La1—La1^{iii}	102.01 (2)	La1—S3—La1^{xi}	150.89 (4)
S3^{iii}—La1—La1^{iii}	46.251 (17)	La1^{ii}—S3—La1^{xi}	84.64 (3)
S2^{ii}—La1—La1^{iii}	172.533 (17)	Zr1—S4—La1^{xii}	90.83 (3)
S2—La1—La1^{iii}	47.425 (16)	Zr1—S4—La1^{vii}	90.83 (3)
La1^{iv}—La1—La1^{iii}	128.467 (9)	La1^{xii}—S4—La1^{vii}	91.36 (3)
La1^{v}—La1—La1^{iii}	90.409 (4)	Zr1—S4—La1^{iii}	106.12 (3)
S4^{i}—La1—La1^{ii}	107.50 (2)	La1^{xii}—S4—La1^{iii}	163.03 (4)
S4^{ii}—La1—La1^{ii}	91.72 (2)	La1^{vii}—S4—La1^{iii}	87.705 (9)
S1^{ii}—La1—La1^{ii}	46.074 (16)	Zr1—S4—La1^{x}	106.12 (3)
S1—La1—La1^{ii}	124.18 (2)	La1^{xii}—S4—La1^{x}	87.705 (9)
S3—La1—La1^{ii}	47.258 (17)	La1^{vii}—S4—La1^{x}	163.03 (4)
S3^{iii}—La1—La1^{ii}	128.91 (2)	La1^{iii}—S4—La1^{x}	88.28 (3)
S2^{ii}—La1—La1^{ii}	48.044 (16)		

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