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Zirconium(IV) dilanthanum(III) pentasulfide

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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{Zr-S}) = 0.001$ 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 isotopic (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) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 14.93$ mm⁻¹ $T = 100$ K $0.12 \times 0.11 \times 0.09$ mm

Data collection

Bruker APEX2 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 $I > 2\sigma(I)$ $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.017$ $wR(F^2) = 0.056$ $S = 2.51$

890 reflections

44 parameters

 $\Delta\rho_{\text{max}} = 2.20$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.54$ 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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supplementary materials

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Comment

Single crystals of ZrLa_2S_5 resulted from attempts to synthesize zirconium analogues of the uranium lanthanide oxysulfide compound $\text{UYb}_2\text{O}_2\text{S}_3$ (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).

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.

Refinement

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

Figures

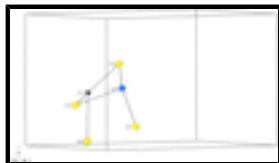


Fig. 1. The asymmetric unit of ZrLa_2S_5 . Displacement ellipsoids are displayed at the 95% probability level.

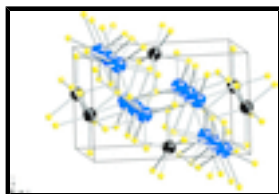


Fig. 2. The ZrLa_2S_5 structure. La atoms are blue, Zr atoms are black, S atoms are yellow

Zirconium(IV) dilanthanum(III) pentasulfide

Crystal data

ZrLa_2S_5	$D_x = 5.061 \text{ Mg m}^{-3}$
$M_r = 529.34$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Orthorhombic, $Pnma$	Cell parameters from 6255 reflections
$a = 11.4784 (4) \text{ \AA}$	$\theta = 3.1\text{--}27.9^\circ$
$b = 8.2010 (3) \text{ \AA}$	$\mu = 14.93 \text{ mm}^{-1}$
$c = 7.3799 (3) \text{ \AA}$	$T = 100 \text{ K}$
$V = 694.70 (5) \text{ \AA}^3$	Prism, black
$Z = 4$	$0.12 \times 0.11 \times 0.09 \text{ mm}$
$F(000) = 936$	

Data collection

Bruker APEXII CCD diffractometer	890 independent reflections
Radiation source: fine-focus sealed tube graphite	877 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.018$
Absorption correction: numerical [face indexed (<i>SADABS</i> ; Bruker, 2009)]	$\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 3.3^\circ$
$T_{\text{min}} = 0.263$, $T_{\text{max}} = 0.340$	$h = -14 \rightarrow 15$
8134 measured reflections	$k = -10 \rightarrow 6$
	$l = -9 \rightarrow 9$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.017$	$[1.00000 + 0.00000\exp(0.00(\sin\theta/\lambda)^2)] / [\sigma^2(F_o^2) + 0.00000 + 0.00000 * P + (0.0158P)^2 + 0.00000\sin\theta/\lambda]$
	where $P = 1.00000F_o^2 + 0.00000F_c^2$

$wR(F^2) = 0.056$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 2.51$	$\Delta\rho_{\max} = 2.20 \text{ e } \text{\AA}^{-3}$
890 reflections	$\Delta\rho_{\min} = -0.54 \text{ e } \text{\AA}^{-3}$
44 parameters	Extinction correction: <i>SHELXL97</i> (Sheldrick, 2008), $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	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 (\AA , $^\circ$)

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)

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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) $x-1/2, -y+1/2, -z+1/2$.

Fig. 1

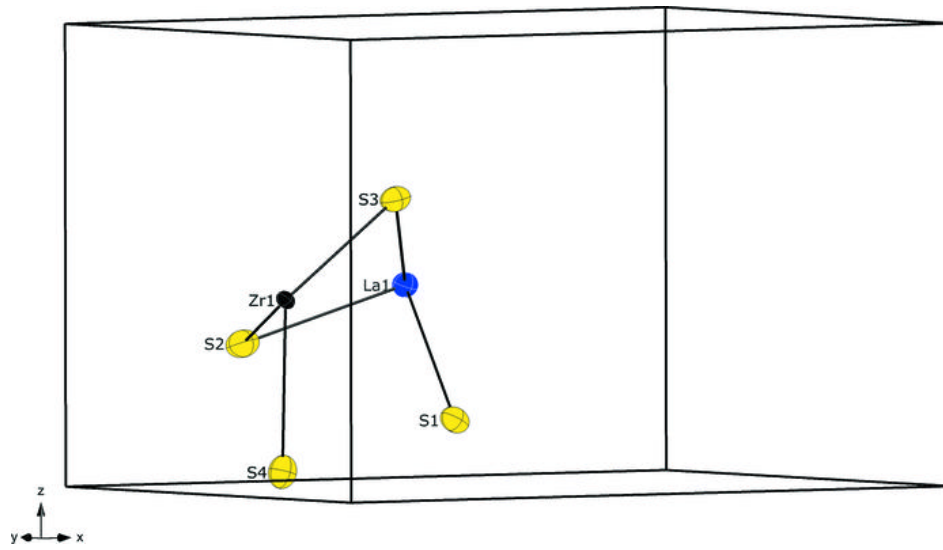


Fig. 2

