

SHORT STRUCTURAL PAPERS

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Caesium Lanthanum Bis(sulphate)

BY NATAŠA BUKOVEC, VENČESLAV KAUČIČ AND LJUBO GOLIC

Department of Chemistry, University Edvard Kardelj, Murnikova 6, 61000 Ljubljana, Yugoslavia

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Abstract. CsLa(SO₄)₂, monoclinic, $P2_1/n$, $a = 7.929$ (1), $b = 5.483$ (1), $c = 17.153$ (1) Å, $\beta = 91.46$ (1)° at 293 (1) K, $Z = 4$, $D_o = 4.19$, $D_c = 4.13$ Mg m⁻³, $V = 745.5$ Å³, $\mu(\text{Mo } K\alpha) = 11.25$ mm⁻¹. The La atom is nine coordinated by O atoms in the form of an irregular polyhedron. The polyhedra together with the S atoms form a layer-like structure parallel to the [101] diagonal. The Cs atoms, which lie between the layers, have a coordination number of thirteen.

Introduction. There are two different structure modifications of compounds CsLn(SO₄)₂ (Ln = La, Pr), which can be prepared by heating CsLn(SO₄)₂·4H₂O with a 4.5 M solution of H₂SO₄ in a sealed tube at 573 K. The structure of CsPr(SO₄)₂ has been solved (Bukovec, Golič, Bukovec & Šiftar, 1978). Both CsPr(SO₄)₂ and CsLa(SO₄)₂ crystallize as thin plates.

Cell dimensions of CsLa(SO₄)₂ were derived by least squares from the positions of 30 high-angle reflections, collected on an Enraf–Nonius CAD-4 automatic diffractometer equipped with a graphite monochromator and using Mo $K\alpha$ radiation. Intensities were recorded with the ω – 2θ scan. The whole sphere of reflections (4335 in all) in the range $1.5 \leq \theta \leq 30.0^\circ$ was measured. The symmetry-related reflections were averaged (mean discrepancy on $I = 5.6\%$) to yield 2141 independent reflections of which 1973 with $I_o \geq 3\sigma(I_o)$ (from counting statistics) were considered observed and used for the analysis. The data were corrected for Lorentz and polarization effects. An absorption correction based on the equations of the crystal faces was also applied to all the reflections.

The structure was solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) to locate the La and Cs atoms and electron density maps to locate the remaining atoms. Refinement of the positional and isotropic thermal parameters gave $R = 0.073$. The structure was then refined with anisotropic temperature factors for all atoms to $R_1 = \sum |F_o| -$

$|F_c| / \sum |F_o| = 0.066$, and $R_2 = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0.073$. The weighting function was determined empirically [weight (F_o) = $wF \times wS$]: $F_o < 30$: $wF = (F_o/30)^{1.0}$; $F_o > 60$: $wF = (60/F_o)^{1.5}$; $30 \leq F_o \leq 60$: $wF = 1.0$; $\sin \theta < 0.35$: $wS = (\sin \theta / 0.35)^2$; $\sin \theta > 0.45$: $wS = (0.45 / \sin \theta)^2$; $0.35 \leq \sin \theta \leq 0.45$: $wS = 1.0$.

Scattering factors for neutral Cs, La, S and O (Cromer & Mann, 1968) with anomalous-scattering coefficients f' and f'' (Cromer & Liberman, 1970) were used. No extinction correction was applied.*

Discussion. The final atomic coordinates are listed in Table 1. The La atom is coordinated to nine O atoms in the form of an irregular polyhedron. Interatomic distances and angles are given in Table 2. There are only small differences between S–O distances in the S(1) sulphate group (Table 3). However, S(2)–O(7) in

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34761 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates ($\times 10^5$ for La, Cs and S; $\times 10^4$ for O) and isotropic thermal parameters

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
La	63082 (7)	80807 (11)	13587 (3)	0.91 (2)
Cs	13626 (8)	26477 (12)	11585 (4)	1.25 (2)
S(1)	67732 (28)	25556 (38)	1977 (13)	0.79 (4)
S(2)	54181 (27)	26275 (39)	24638 (13)	0.70 (4)
O(1)	7987 (10)	578 (15)	367 (5)	1.24 (16)
O(2)	7451 (10)	4904 (14)	489 (5)	1.20 (15)
O(3)	5224 (10)	1945 (17)	619 (5)	1.47 (17)
O(4)	6423 (10)	2733 (15)	–646 (5)	1.17 (15)
O(5)	4376 (10)	510 (14)	2227 (5)	1.21 (15)
O(6)	4723 (10)	4882 (14)	2126 (5)	1.29 (16)
O(7)	7167 (9)	2204 (16)	2178 (5)	1.10 (15)
O(8)	5543 (10)	2826 (16)	3316 (4)	1.13 (15)

Table 2. *Interatomic distances (Å) and angles (°)*

La polyhedron

La—O(2)	2.480 (8)	La—O(7 ^I)	2.739 (8)
La—O(6)	2.544 (8)	La—O(4 ^{II})	2.500 (8)
La—O(1 ^I)	2.580 (8)	La—O(7 ^{III})	2.801 (8)
La—O(3 ^I)	2.605 (9)	La—O(8 ^{III})	2.549 (8)
La—O(5 ^I)	2.541 (8)		
O(2)—La—O(6)	91.1 (3)	O(1 ^I)—La—O(4 ^{II})	103.2 (3)
O(2)—La—O(1 ^I)	76.9 (3)	O(1 ^I)—La—O(7 ^{III})	117.6 (2)
O(2)—La—O(3 ^I)	113.5 (3)	O(1 ^I)—La—O(8 ^{III})	69.8 (3)
O(2)—La—O(5 ^I)	162.9 (3)	O(3 ^I)—La—O(5 ^I)	70.3 (3)
O(2)—La—O(7 ^I)	143.0 (3)	O(3 ^I)—La—O(7 ^I)	69.7 (3)
O(2)—La—O(4 ^{II})	84.6 (3)	O(3 ^I)—La—O(4 ^{II})	68.6 (3)
O(2)—La—O(7 ^{III})	105.2 (3)	O(3 ^I)—La—O(7 ^{III})	134.9 (3)
O(2)—La—O(8 ^{III})	73.9 (3)	O(3 ^I)—La—O(8 ^{III})	117.4 (3)
O(6)—La—O(1 ^I)	167.7 (3)	O(5 ^I)—La—O(7 ^I)	54.0 (2)
O(6)—La—O(3 ^I)	130.7 (3)	O(5 ^I)—La—O(4 ^{II})	81.5 (3)
O(6)—La—O(5 ^I)	75.2 (3)	O(5 ^I)—La—O(7 ^{III})	79.5 (2)
O(6)—La—O(7 ^I)	115.1 (3)	O(5 ^I)—La—O(8 ^{III})	120.2 (2)
O(6)—La—O(4 ^{II})	72.3 (3)	O(7 ^I)—La—O(4 ^{II})	126.8 (2)
O(6)—La—O(7 ^{III})	68.0 (3)	O(7 ^I)—La—O(7 ^{III})	65.5 (2)
O(6)—La—O(8 ^{III})	110.1 (3)	O(7 ^I)—La—O(8 ^{III})	72.8 (2)
O(1 ^I)—La—O(3 ^I)	54.3 (3)	O(4 ^{II})—La—O(7 ^{III})	139.2 (2)
O(1 ^I)—La—O(5 ^I)	115.9 (3)	O(4 ^{II})—La—O(8 ^{III})	158.3 (3)
O(1 ^I)—La—O(7 ^I)	76.9 (2)	O(7 ^{III})—La—O(8 ^{III})	52.8 (2)

Cs polyhedron

Cs—O(3)	3.245 (8)	Cs—O(1 ^v)	3.211 (8)
Cs—O(5)	3.197 (8)	Cs—O(4 ^v)	3.556 (8)
Cs—O(6)	3.336 (8)	Cs—O(5 ^v)	3.250 (8)
Cs—O(1 ^{iv})	3.179 (8)	Cs—O(8 ^v)	3.351 (8)
Cs—O(2 ^{iv})	3.506 (8)	Cs—O(6 ^{vii})	3.440 (8)
Cs—O(2 ^{II})	3.288 (9)	Cs—O(8 ^{vii})	3.187 (8)
Cs—O(4 ^{II})	3.218 (8)		

Symmetry code

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

Table 3. *Bond distances (Å) and angles (°) of the SO₄ groups*

S(1)—O(1)	1.475 (8)	S(2)—O(5)	1.476 (8)
S(1)—O(2)	1.478 (8)	S(2)—O(6)	1.467 (8)
S(1)—O(3)	1.479 (9)	S(2)—O(7)	1.501 (8)
S(1)—O(4)	1.470 (8)	S(2)—O(8)	1.467 (8)
O(1)—S(1)—O(2)	110.1 (5)	O(5)—S(2)—O(6)	110.6 (5)
O(1)—S(1)—O(3)	106.5 (5)	O(5)—S(2)—O(7)	107.7 (5)
O(1)—S(1)—O(4)	110.4 (5)	O(5)—S(2)—O(8)	110.9 (5)
O(2)—S(1)—O(3)	109.4 (5)	O(6)—S(2)—O(7)	110.0 (5)
O(2)—S(1)—O(4)	109.5 (5)	O(6)—S(2)—O(8)	110.3 (5)
O(3)—S(1)—O(4)	110.9 (5)	O(7)—S(2)—O(8)	107.4 (4)

the S(2) sulphate group is rather longer than the others because O(7) is a bridging atom between two La atoms. The La—O(7)—La angle is 134.2 (3)° and O(7)—La bond distances are 2.739 (8) and 2.801 (8) Å. Smaller angles O(1)—S(1)—O(3), O(5)—S(2)—O(7) and O(7)—S(2)—O(8) result from the bonding of O atoms to the

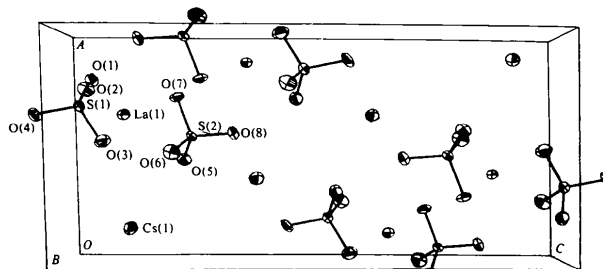


Fig. 1. A view of the unit cell.

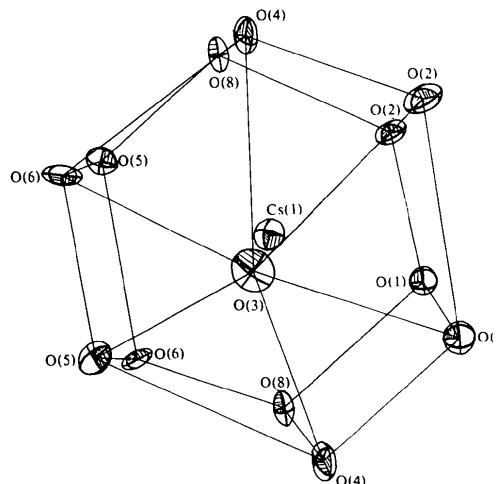


Fig. 2. The coordination polyhedron of caesium.

same La atoms. Thus each sulphate group is bonded to three La atoms. The sulphate groups join La polyhedra into infinite layers parallel to the [101] diagonal (Fig. 1).

The Cs atoms lie between the layers and are coordinated with thirteen O atoms (Fig. 2). The coordination polyhedron around Cs is in the form of two parallel sixfold rings; one of them is centred. This can be compared with the Cs polyhedron in CsPr(SO₄)₂, where both sixfold rings are centred and the coordination number is fourteen.

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