

The Crystal Structure of Cesium Sulfate, β -Cs₂SO₄

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The crystal structure of the room temperature modification of cesium sulfate, β -Cs₂SO₄, has been studied by X-ray diffraction techniques. At 25 °C the orthorhombic (*Pnam*) unit cell has the dimensions: $a=8.239(1)$, $b=10.944(1)$, and $c=6.258(1)$ Å; $Z=4$ and $d_{\text{calc}}=4.260$ g cm⁻³. The structure has been refined by least squares to $R=0.038$ on the basis of 1330 independent reflections. The cesium ions are surrounded by eleven or by nine oxygen atoms with average metal-oxygen distances of 3.309(2) and 3.188(2) Å, respectively. The sulfate tetrahedra are almost regular with an average S—O distance of 1.477(2) Å. The compound is isostructural with β -K₂SO₄ and β -Rb₂SO₄.

The first X-ray diffraction studies of alkali sulfates were reported in 1916 by Ogg and Hopwood.¹ They had determined the unit cell dimensions for (NH₄)₂SO₄, β -K₂SO₄, β -Rb₂SO₄, and β -Cs₂SO₄, and thereby verified Tutton's suggestion² that the four sulfates were isomorphous. Later (in 1928) Ogg published a paper on the crystal structure of the four isomorphous sulfates.³ The structures of (NH₄)₂SO₄ and β -K₂SO₄ have been reexamined several times, whereas a redetermination of the β -Rb₂SO₄ structure has not been carried out until recently.⁴ A precise determination of the β -Cs₂SO₄ structure is reported in this investigation, which is a part of a program concerning the dimensions of the sulfate ion and the configuration of alkali-oxygen polyhedra.⁴⁻⁸

EXPERIMENTAL

The crystals used in this investigation were of *pro analysi* quality from Merck, Darmstadt. The X-ray powder pattern of the sample was in good agreement with the data published by Pannetier, Gaultier, and Tabrizi.⁹ Values for the unit cell dimensions were calculated from

the reflections of a photograph taken at 25 °C with strictly monochromatized CuK α radiation ($\lambda=1.5405$ Å) in a Guinier-Hägg type focusing camera. Potassium chloride ($a=6.29294$ Å)¹⁰ was used as an internal standard. The intensities and positions of the reflections on the photograph were determined by use of a computer-controlled SAAB film scanner and associated programs.¹¹ The lattice parameters were refined from 27 single-indexed reflections by the method of least squares as implemented in the program PIRUM.¹² The dimensions of the orthorhombic (*Pnam*) unit cell at 25 °C are: $a=8.239(1)$, $b=10.944(1)$, $c=6.258(1)$ Å, and $V=564.2$ Å³. $Z=4$ gives a calculated density of 4.260 g cm⁻³. The values above are very close to those given by Pannetier *et. al.*:⁹ *i.e.* $a=8.235(1)$, $b=10.940(3)$, and $c=6.257(1)$ Å at room temperature.

Single crystal data. Single crystals of β -Cs₂SO₄ were prepared by the evaporation of an aqueous solution of the salt at about 0 °C over one week. The crystals were filtered off and washed with cold water. A small prismatic crystal with the approximate dimensions 0.07 × 0.045 × 0.12 mm in the axial directions was mounted along the *c* axis and used for the collection of the intensity data.

The systematic absences are: $h0l$, $h \neq 2n$; and $0kl$, $k+l \neq 2n$, which is characteristic of the space group *Pna*2₁ and its centrosymmetric equivalent *Pnam*. Since β -Rb₂SO₄ (*cf.* Ref. 4) as well as β -K₂SO₄ (*cf.* Ref. 13) belong to space group *Pnam*, there is very little reason to believe that this should not be so for β -Cs₂SO₄ too. Moreover, the $N(z)$ test¹⁴ applied to the complete data set clearly indicated a centric distribution. The space group *Pnam* (No. 62) was therefore chosen as the most probable.

Single-crystal data were collected on a Siemens automatic four-circle diffractometer equipped with a scintillation detector and a graphite monochromator, with MoK α radiation ($\lambda=0.7107$ Å). The $\theta-2\theta$ scan technique was employed, with the five-values measuring procedure. The count was taken in steps of 0.01° with a step time of 1.2 s. Three strong reflections were measured every 5 h. Their

Table 1. Atomic coordinates and temperature factors for β - Cs_2SO_4 ($Pn\bar{m}$). General equivalent positions $8(d)$: $\pm(x, y, z)$; $\pm(-x, -y, \frac{1}{2}+z)$; $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z)$; $\pm(\frac{1}{2}-x, \frac{1}{2}+y, -z)$. The estimated standard deviations (within parentheses) refer to the last digit of the respective values. The anisotropic temperature factors are of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The B_{ij} values below are multiplied by 10^4 .

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cs(1)	0.6771(1)	0.4093(1)	$\frac{1}{2}^a$	70(1)	36(1)	92(1)	-1(1)	0 ^a	0 ^a
Cs(2)	-0.0112(1)	0.7015(1)	$\frac{1}{2}^a$	55(1)	35(1)	108(1)	1(1)	0 ^a	0 ^a
S	0.2411(2)	0.4172(1)	$\frac{1}{2}^a$	44(2)	23(1)	64(2)	0(1)	0 ^a	0 ^a
O(1)	0.0620(6)	0.4127(5)	$\frac{1}{2}^a$	34(5)	54(4)	217(15)	0(4)	0 ^a	0 ^a
O(2)	0.2973(7)	0.5460(4)	$\frac{1}{2}^a$	87(6)	25(3)	121(10)	-8(3)	0 ^a	0 ^a
O(3)	0.3035(4)	0.3558(3)	0.0570(5)	90(4)	40(2)	100(7)	4(2)	24(5)	-19(3)

^a Parameter fixed by symmetry.

intensity variations lay within $\pm 1\%$ during the complete run. All lattice points with $h, k, l \geq 0$ and $5^\circ \leq \theta \leq 35^\circ$ were measured. Of the 1330 independent non-extinct reflections, 803 (60%) had $\sigma(I)/I \leq 0.10$ while 185 (14%) had $\sigma(I)/I > \frac{1}{2}$ [$\sigma(I)/I$ is defined as $(I_{\text{tot}} + I_{\text{back}})^{1/2} / (I_{\text{tot}} - I_{\text{back}})^{1/2}$]. The net intensities were corrected for Lorentz, polarization, and absorption ($\mu = 133 \text{ cm}^{-1}$) effects with the program DATAPH (Coppens, Leiserowitz, Rabinovich, and Hamilton). The transmission factor A ($I = I_{\text{obs}}/A$) ranged from 0.350 to 0.567.

A general survey of the IBM 360/75 computer programs used in this work has been reported.¹⁵

STRUCTURE REFINEMENT

The structure was refined with the atomic parameters of rubidium sulfate⁴ as a start. The program FALFA was used for the refinement; it is a local modification¹⁶ of the full-matrix least-squares program LINUS (Busing, Martin, Levy, Hamilton, and Ibers). The atomic scattering factors for Cs^+ , S^0 , and O^- , with corrections for the real and imaginary part of the anomalous dispersion, were taken from the *International Tables*.¹⁷⁻¹⁸

The R value, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, dropped to 0.069 for the isotropic model and to 0.058 for the anisotropic model. However, inspection of the structure factor list showed that extinction effects were pronounced for some of the strongest, low-angle reflections. The most severe extinction occurred for the reflections (002) [$Q = |F_o|/|F_c| = 0.52$], (031) [$Q = 0.61$], (004), [$Q = 0.67$], and (211) [$Q = 0.67$].

From this stage, an isotropic secondary extinction parameter g ¹⁹ was included in the

refinement, and the R value dropped to 0.038 for the model with anisotropic temperature factors. The refined value of the parameter g was 0.54 ± 0.04 . The discrepancy between the observed and calculated structure factors for the above-mentioned four reflections decreased considerably [e.g. for reflection (002), $Q = 0.956$]. Refinements including anisotropic secondary extinction parameters¹⁹ were also performed. However, the large correlation coefficients now appearing between some of the refined parameters, in addition to the insignificant improvement of the result, lead the author

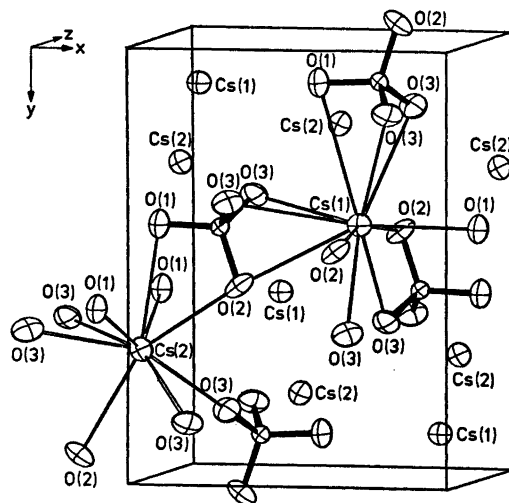


Fig. 1. ORTEP plot of the β - Cs_2SO_4 structure. The small ellipsoids represent sulfur atoms. For clarity only two cesium-oxygen polyhedra are shown.

Table 2. Interatomic distances (Å) and angles (°). Standard deviations are quoted in parentheses. All Cs—O distances < 4.2 Å are given below. The S—O distances in square brackets have been corrected for thermal vibrations of the atoms according to the riding-motion model.²²

Cs(1)—O(1)		3.172(5)		Cs(2)—O(2)		3.059(5)
—O(2)	(× 2)	3.174(2)		—O(3)	(× 2)	3.077(3)
—O(3)	(× 2)	3.213(3)		—O(3')	(× 2)	3.144(3)
—O(3')	(× 2)	3.311(3)		—O(2')		3.182(5)
—O(3'')	(× 2)	3.358(3)		—O(1)		3.218(6)
—O(2')		3.468(6)		—O(1')	(× 2)	3.395(2)
—O(1')		3.649(6)		Average:		3.188(2)
Average:		3.309(2)				
S—O(1)		1.476(5)	[1.493]	O(1)—O(2)		2.426(7)
S—O(2)		1.484(5)	[1.493]	O(1)—O(3)	(× 2)	2.409(5)
S—O(3)	(× 2)	1.475(3)	[1.486]	O(2)—O(3)	(× 2)	2.407(5)
Average:		1.477(2)	[1.490]	O(3)—O(3')		2.416(6)
				Average:		2.412(3)
O(1)—S—O(2)		110.1(3)				
O(1)—S—O(3)	(× 2)	109.5(2)				
O(2)—S—O(3)	(× 2)	108.9(2)				
O(3)—S—O(3')		110.0(3)				
Average:		109.5(1)				

Table 3. Comparison among three isostructural compounds β -M₂SO₄ (M = K, Rb, and Cs). Values calculated by the author from parameters given in Refs. 4 and 13 are denoted by asterisks.

Compound	β -K ₂ SO ₄ ^a	β -Rb ₂ SO ₄ ^b	β -Cs ₂ SO ₄ ^c
Unit cell dimensions			
<i>a</i> (Å)	7.476(3)	7.813(1)	8.239(1)
<i>b</i> (Å)	10.071(4)	10.426(2)	10.944(1)
<i>c</i> (Å)	5.763(2)	5.969(1)	6.258(1)
<i>V</i> (Å ³)	433.9*	486.2*	564.2
Uncorrected distances (Å)			
Metal-oxygen			
M(1)—O, average (11-coord.)	3.030(2)*	3.143(3)	3.309(2)
M(2)—O, average (9-coord.)	2.865(2)*	3.003(3)	3.188(2)
Sulfur-oxygen			
S—O(1)	1.459(4)	1.492(9)	1.476(5)
S—O(2)	1.473(4)	1.473(9)	1.484(5)
S—O(3) (× 2)	1.472(5)	1.466(7)	1.475(3)
S—O average distance	1.469(2)	1.474(4)	1.477(2)
Oxygen-oxygen			
Average O—O in the SO ₄ group	2.399(2)*	2.408(5)*	2.412(3)
Corrected distances (Å)			
Riding-motion model,			
S—O average distance	1.481*	1.487	1.490
R.m.s. radial thermal displacements (Å)			
M(1)	0.262*	0.236*	0.253
M(2)	0.249*	0.251*	0.247
S	0.211*	0.183*	0.204
O(1)	0.293*	0.280*	0.296
O(2)	0.273*	0.266*	0.263
O(3)	0.291*	0.272*	0.274

^a Ref. 13. ^b Ref. 4. ^c This work.

to regard the isotropic-extinction model as the most reliable one. In this refinement Hughes' weighting function²⁰ with $h=4$ and $F_{o,\min}=20$ was used for the 1145 "significant" reflections with $\sigma(I)/I \leq \frac{1}{2}$, while zero weights were assigned to the 185 "insignificant" reflections with $\sigma(I)/I > \frac{1}{2}$. The atomic parameters obtained in the refinement are listed in Table 1. The structure factor list can be obtained at request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The present work shows that Ogg's atomic positions⁹ from 1928 were essentially correct. β -Cs₂SO₄ is isostructural with β -Rb₂SO₄, β -K₂SO₄, and many other compounds.²¹ An ORTEP²² plot of the structure is shown in Fig. 1. The structure is pseudo-hexagonal with $b/c = 1.7488 \approx 3\frac{1}{2}$.

Some interatomic distances (uncorrected) and angles are listed in Table 2. The S—O distances have also been corrected for the thermal vibrations of the atoms according to the riding-motion model²³ by use of the program ORFFE (Busing, Martin, and Levy). The sulfate tetrahedra are almost regular with an average S—O distance of 1.477(2) Å (uncorrected). They have a crystallographically imposed m symmetry. The cesium ions are surrounded in an irregular way by either eleven or nine oxygen atoms. The average Cs—O distances are 3.309(2) Å (11-coordination) and 3.188(2) Å (9-coordination), respectively.

Table 3 contains a comparison of the three isostructural compounds β -K₂SO₄ (Ref. 13), β -Rb₂SO₄ (Ref. 4), and β -Cs₂SO₄ (this work). It comprises the unit cell dimensions, some interatomic distances, and the r.m.s. radial thermal displacements of the atoms. The table shows a strong correlation between the increase in metal-oxygen distances and the increase in unit cell dimensions. As the metal-oxygen distances increase about 5%, there is a corresponding increase in the order of 4–6% for each unit cell edge. There is also a slight, though hardly significant, indication that the dimensions of the sulfate ions should increase a little as the size of the cations in the β -M₂SO₄ structure increases. An accurate structure analysis of the isostructural compound Tl₂SO₄,

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where the cations are about the same size as Rb⁺, might be of interest in this respect.

The r.m.s. radial thermal displacements are rather similar for all crystallographically analogous atoms in the three β -M₂SO₄ structures; the analogous atoms vibrate almost identically. It should be noted, however, that the reflection data for β -K₂SO₄ were not corrected for absorption [$\mu(\text{MoK}\alpha) = 24.9 \text{ cm}^{-1}$].¹³ The data for β -Rb₂SO₄ have been treated in almost the same manner as described here for β -Cs₂SO₄.

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