

## Pentapotassium sodium hexasulfatodicerate(III)

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## Key indicators

Single-crystal X-ray study

T = 173 K

Mean  $\sigma(S-O) = 0.002 \text{ \AA}$ 

R factor = 0.020

wR factor = 0.051

Data-to-parameter ratio = 21.0

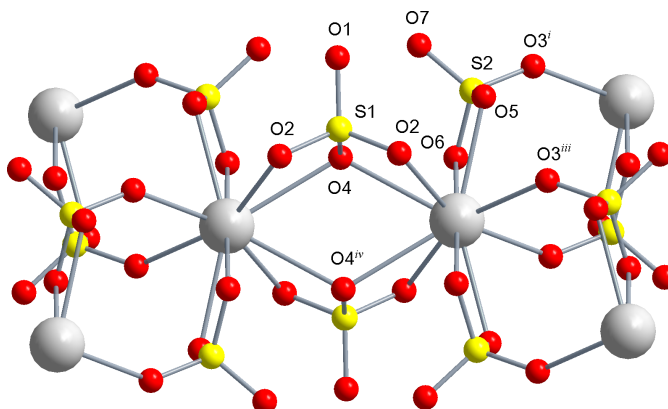
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

$K_5Na[Ce_2(SO_4)_6]$  contains two  $Ce^{III}$  ions, cross-linked *via* two oxygen and four sulfate bridges, a unique configuration for cerium sulfates. Each cerium is (8 + 2)-coordinated by O atoms of four sulfate groups by bidentate linkages.

## Comment

Various cerium sulfates have been described in the last three decades. The most common coordination numbers of cerium are eight and nine. Cerium ions are connected *via* different kinds of oxygen bridges. The most common cross-linkage is through a sulfate group, whose tetrahedron shares corners with two cerium polyhedra,  $Ce-O-S-O-Ce$ . Another kind of cross-linkage occurs by bidentate coordination of oxygen through sulfate groups,  $Ce-O-S-O-Ce$  (Dereigne *et al.*, 1972) or oxo anions,  $Ce-O-Ce$  (Lindgren, 1976). Bidentate connection to the sulfate group is common and the  $Ce-O_2-S-O_2$  coordination can be described as a 'petal of a flower'. The number of petals varies from two (Kuznetsov *et al.*, 1986) to four (Shan & Huang, 1998). This formation results in edge-sharing of a cerium polyhedron and a sulfate tetrahedron.

In the crystal structure of the title compound, there are two Ce atoms that are cross-linked through two oxygen bridges and two sulfate bridges (Fig. 1). This is a unique configuration for cerium sulfates. The two oxygen bridges form a plane shared by the cerium coordination polyhedra. The bonding distance of  $Ce-O4$  is 2.724 (1) Å, which is considered too long, but can be explained by the three coordinated O4 atoms having a bridging nature to two sulfate groups. Although three-coordination is more frequent for an O atom in water molecules, this phenomenon has been observed in other cerium sulfates (Dereigne *et al.*, 1972). As a result of these two kinds of bridges, a binuclear unit is formed and it shares a total

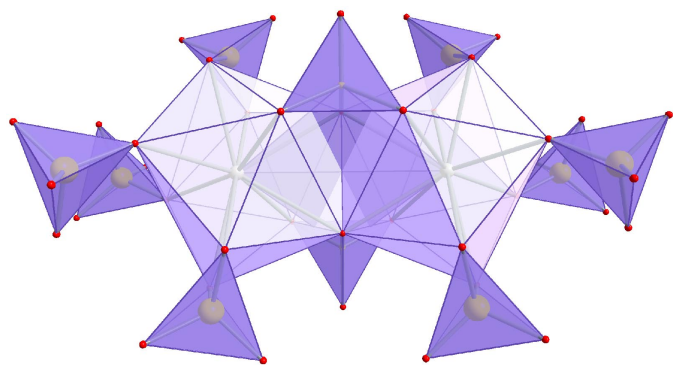


**Figure 1**  
Part of the structure of  $[Ce_2(SO_4)_6]^{4-}$ , with the large spheres representing cerium.

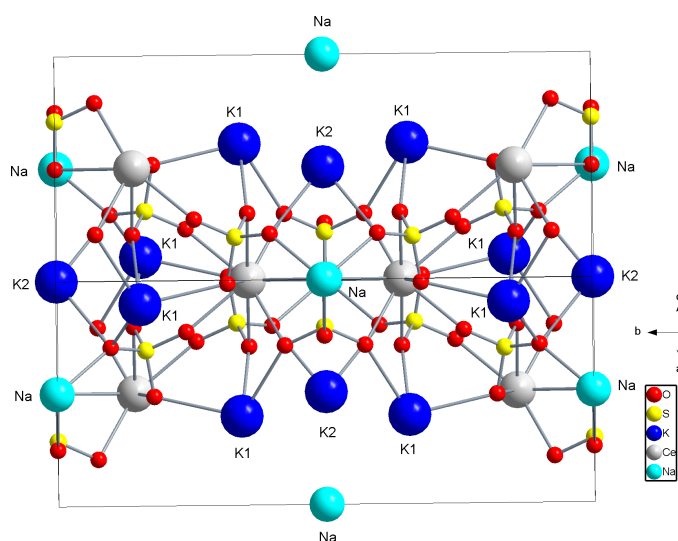
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**Figure 2**  
The linked coordination polyhedra of  $[\text{Ce}_2(\text{SO}_4)_6]^{4-}$ .



**Figure 3**  
The network of cerium sulfate units surrounded by alkali metal ions.

of six sulfate groups with surrounding units. Each cerium is (8 + 2)-coordinated by O atoms, and the Ce–O coordination includes four bidentate sulfate units, where two sulfate groups are also shared by the other Ce atoms. This is illustrated with two sulfate tetrahedra, which share two edges on each side with the binuclear cerium polyhedra (Fig. 2). The remaining sulfate tetrahedra share all corners with cerium polyhedra. The sulfate cross-linkage forms an infinite system of cerium binuclear units along the *a* axis; this is surrounded by two layers of alkali metal counter-ions, one on each side.

## Experimental

$\text{Ce}^{\text{IV}}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (1.5 g, 3.75 mmol) was dissolved in water (10 ml) and precipitated with 15 M ammonia, in the expectation of forming  $\text{Ce}(\text{OH})_4$ . The product was washed with water and then dissolved in 12 M HCl. The cerium solution was mixed with  $\text{K}_2\text{CrO}_4$ . After the mixture was allowed to evaporate, plate-shaped light-yellow single crystals were formed. ESEM/EDX analysis revealed sulfur and sodium, which were traced to the starting materials  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{K}_2\text{CrO}_4$  (presumably impure), respectively. The crystals were identified as  $\text{K}_5\text{Na}[\text{Ce}_2(\text{SO}_4)_6]$  by X-ray diffraction.

## Crystal data

$\text{K}_5\text{Na}[\text{Ce}_2(\text{SO}_4)_6]$   
 $M_r = 1075.09$   
 Monoclinic,  $C2/m$   
 $a = 9.2117$  (2) Å  
 $b = 16.3725$  (4) Å  
 $c = 7.7207$  (2) Å  
 $\beta = 111.059$  (1)°  
 $V = 1086.65$  (5) Å<sup>3</sup>  
 $Z = 2$

$D_x = 3.286$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 7272 reflections  
 $\theta = 2.5$ – $32.9^\circ$   
 $\mu = 5.81$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Plate, yellow  
 $0.30 \times 0.10 \times 0.05$  mm

## Data collection

Siemens SMART 1K CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)  
 $T_{\text{min}} = 0.269$ ,  $T_{\text{max}} = 0.745$   
 9019 measured reflections

1998 independent reflections  
 1852 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.032$   
 $\theta_{\text{max}} = 32.9^\circ$   
 $h = -14 \rightarrow 13$   
 $k = -24 \rightarrow 24$   
 $l = -11 \rightarrow 11$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.020$   
 $wR(F^2) = 0.051$   
 $S = 1.06$   
 1998 reflections  
 95 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 2.4852P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 1.28$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -1.87$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å).

Ce1–O3 <sup>i</sup>	2.4953 (17)	Ce1–O6	2.6594 (18)
Ce1–O3 <sup>ii</sup>	2.4953 (17)	Ce1–O4 <sup>iv</sup>	2.7244 (12)
Ce1–O2 <sup>iii</sup>	2.5225 (16)	Ce1–O4	2.7244 (12)
Ce1–O2	2.5225 (16)	S1–O1	1.459 (2)
Ce1–O5	2.6172 (17)	S1–O2 <sup>v</sup>	1.4904 (16)
Ce1–O5 <sup>iii</sup>	2.6172 (17)	S1–O2	1.4904 (16)
Ce1–O6 <sup>iii</sup>	2.6594 (18)	S1–O4	1.494 (2)

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

Atom K2 shows rather large displacement parameters. An attempt was made to split the site, but the refinement was unstable. Both the highest peak and the deepest hole on the difference electron-density map are situated in the vicinity of atom K2, at distances of 1.13 and 0.48 Å, respectively.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *SADABS* (Sheldrick, 2002); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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