

## A pseudo-merohedrally twinned rare-earth sulfate: $\text{K}_6[\text{Ce}(\text{HSO}_4)_2(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$ , a novel structure type

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A novel structure type of an acidic rare-earth sulfate, hexapotassium cerium dihydrogensulfate tetrasulfate monohydrate, is reported. The crystal is twinned, mimicking tetragonal symmetry. The  $\text{Ce}^{\text{IV}}$  atom is nine-coordinate, connecting to one corner-sharing and four edge-sharing sulfate groups. One of the potassium ions is disordered over two general positions. The compound is unique as it contains rare-earth monomers,  $[\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^{5-}$ . The structure is composed of these monomers, water molecules, discrete hydrogensulfate ions and potassium ions held together by ionic interactions. There are two types of alternating layers in the structure, with compositions  $[\text{K}_4\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^-$  and  $[\text{K}_2(\text{HSO}_4)(\text{H}_2\text{O})]^+$ .

### Comment

The chemistry of the lanthanides has expanded rapidly; the interest in their complexes is driven by their promising utilization as a result of their low toxicity. Among the lanthanide materials, cerium compounds have attracted attention owing to their applications as ion conductors, catalysts, and magnetic and fluorescence materials. Recently, during investigations of rare-earth frameworks, advances in the syntheses of new inorganic materials with interesting applications have been achieved (Yu *et al.*, 2004; Perles *et al.*, 2005; He *et al.*, 2005). A comprehensive review of the lanthanide compounds with complex inorganic anions was presented by Wickleder (2002), covering the structurally characterized compounds to that time. These materials are intriguing because of the complexity of their structural arrangements with high coordination numbers and a variety of coordination geometries.

There exists structural information on anhydrous ternary rare-earth sulfates,  $AM(\text{SO}_4)_2$ , with all alkali ions ( $A^+$ ) for nearly the whole lanthanide series (Wickleder, 2002). The most common hydrated ternary rare-earth sulfates are mono- and tetrahydrates; for the smaller  $A^+$  ions the monohydrates

dominate, while for the larger monovalent ions the tetrahydrates prevail. Anhydrous as well as hydrated ternary sulfates with  $A^+M^{3+}$  compositions other than 1:1 are not well characterized, although a number of phases are supposed to exist (Wickleder, 2002). Nearly all the structurally characterized sulfates with an  $A:M$  ratio not equal to 1 are described as non-centrosymmetric (Wickleder, 2002). Five hydrated alkali cerium sulfates have been structurally characterized to date, *viz.* one  $\text{Ce}^{\text{IV}}$  compound,  $\text{K}_2\text{Ce}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$  (Iskhakova *et al.*, 1988), and four  $\text{Ce}^{\text{III}}$  compounds,  $A\text{Ce}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$  [ $A = \text{Li}$  (Iskhakova *et al.*, 1987),  $\text{Na}$  (Blackburn & Gerkin, 1995),  $\text{K}$  (Jemmali *et al.*, 2005) and  $\text{Rb}$  (Robinson & Jasty, 1998)]. Ternary rare-earth sulfates with a composition ratio

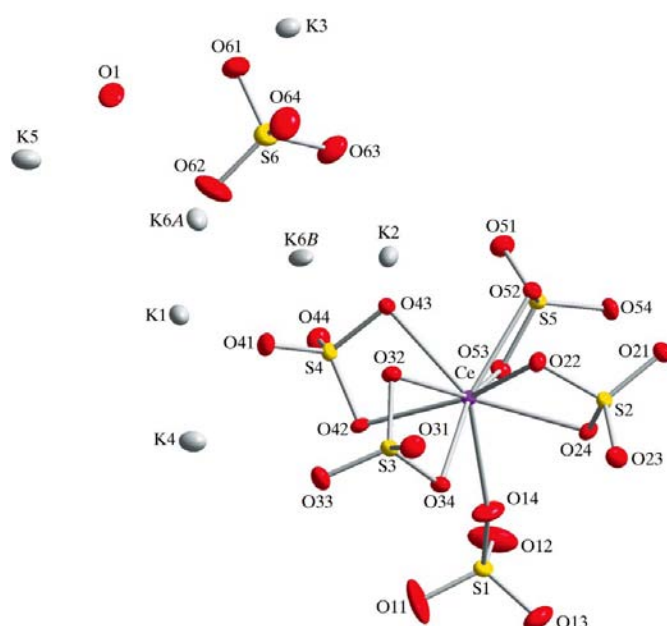


Figure 1

The atom-numbering scheme for the title compound. One of the potassium ions ( $\text{K6A}$  and  $\text{K6B}$ ) is disordered, occupying 50% of two general positions. Displacement ellipsoids are shown at the 30% probability level.

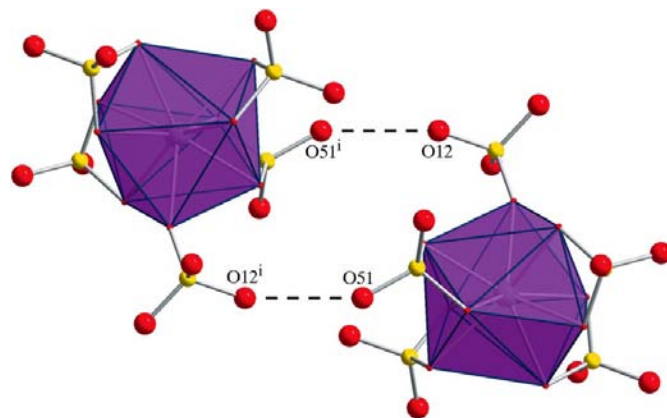
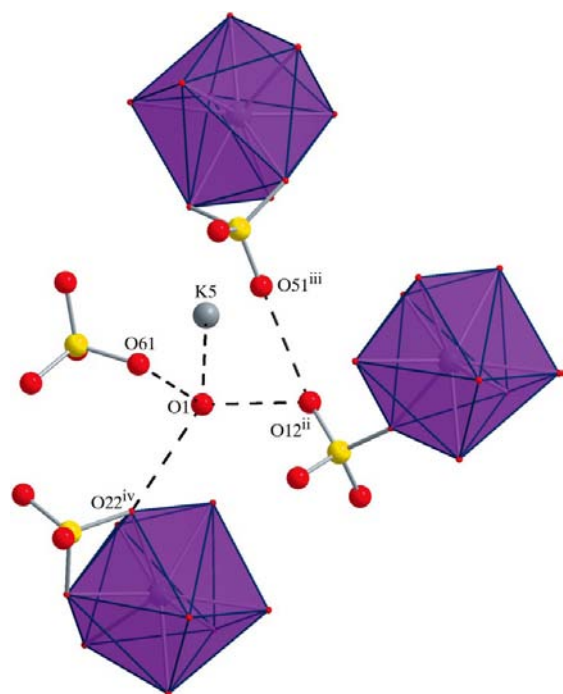


Figure 2

Hydrogen-bonding contacts between hydrogensulfate and sulfate groups, forming dimers of cerium sulfate complexes. The  $\text{O12} \cdots \text{O51}^i$  distance is 2.878 (8) Å. [Symmetry code: (i)  $-x + 1, -y, -z + 1$ ].

$A^+ \cdot M^{3+} > 3$  are very rare and only one structure has been described, *viz.*  $(\text{NH}_4)_8[\text{Ce}_2(\text{SO}_4)_8] \cdot 4\text{H}_2\text{O}$  (Shan & Huang, 1998).

The structure of  $\text{K}_6[\text{Ce}(\text{HSO}_4)_2(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$  is presented here. Crystals are pseudo-merohedrally twinned, mimicking tetragonal symmetry (see *Experimental* for details). There are six potassium ions, one Ce atom, two hydrogensulfate groups, four sulfate groups and one water molecule in the asymmetric unit (Fig. 1). One of the potassium ions (K6A and K6B) is disordered, occupying 50% of two general positions. The Ce atom is coordinated by nine O atoms, belonging to one corner-sharing (S1) and four edge-sharing sulfate groups (S2–S5) (Fig. 1). The cerium coordination polyhedron is a monocapped tetragonal antiprism. Ninefold coordination is not as frequent as eightfold coordination for the  $\text{Ce}^{\text{IV}}$  ion. The Ce–O distances average 2.41 (4) Å (Table 1). The bond-valence sum is 3.84 valence units [using parameters from Trzesowska *et al.* (2006)]. The potassium ions are in contact with seven or eight O atoms at distances ranging between 2.714 (6) and 3.294 (8) Å. The bridging sulfate O atoms are in contact with one potassium ion, while the terminal sulfate O atoms are in contact with two or three potassium ions. The S–O distances within the six sulfate groups average 1.48 (2) Å (Table 1) and the edge-sharing groups (S2–S4) show a departure from the ideal tetrahedral symmetry, with angles ranging from 100.6 (2) to 113.5 (3)°. It is difficult to discern, analyzing the S–O bond lengths, which two of the six sulfate groups are protonated. The structural units present are a  $[\text{Ce}(\text{SO}_4)_5]^{6-}$  unit, one

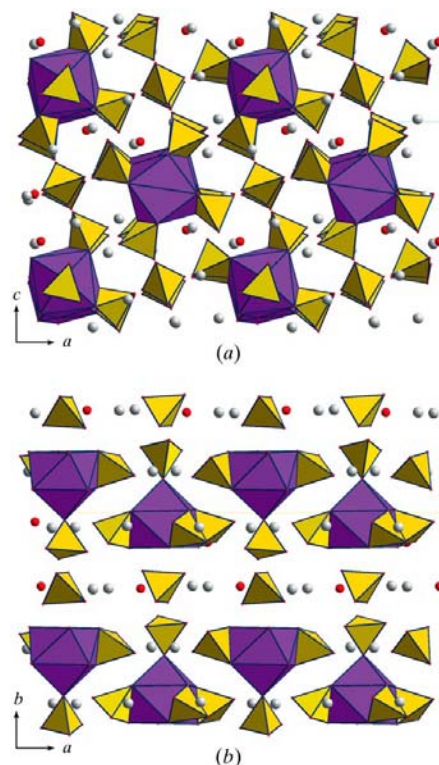


**Figure 3**

Hydrogen-bonding contact possibilities for the hydroxide group (O61) and the water molecule (O1). The  $\text{O61} \cdots \text{O1} \cdots \text{O12}^{\text{ii}}$ ,  $\text{O12}^{\text{ii}} \cdots \text{O1} \cdots \text{O22}^{\text{iv}}$  and  $\text{O22}^{\text{iv}} \cdots \text{O1} \cdots \text{O61}$  angles are 98.6 (2), 121.8 (2) and 90.60 (19)°, respectively, and the  $\text{O1} \cdots \text{O12}^{\text{ii}}$ ,  $\text{O1} \cdots \text{O22}^{\text{iv}}$  and  $\text{O1} \cdots \text{O61}$  distances are 2.642 (7), 2.865 (6) and 2.680 (8) Å, respectively. [Symmetry codes: (ii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $x, y, z + 1$ .]

sulfate ion, six potassium ions and one water molecule, with two of the sulfate ions monoprotonated. From a chemical point of view, we expect the highly electronegative cerium complex to be protonated. From a structural point of view, we assume that one of the H atoms is situated between O51 and O12<sup>i</sup>, forming dimers (symmetry code as in Fig. 2). However, since there is no clear evidence present in the sulfur–oxygen bond lengths, the location of this H atom may be disordered between the S1 and S5 sulfate groups. The other H atom may be located on the S6 sulfate group and attached to O61. The S6–O61 bond length is 1.525 (6) Å, while the remaining S6–O bond lengths average 1.475 (7) Å. The distance between the donor O61 atom and the acceptor water molecule (O1) is 2.680 (8) Å and the S6–O61–O1 angle is 109.2 (3)° (Fig. 3). The water molecule, in contact with one potassium ion (K5), forms hydrogen-bonding contacts to O12<sup>ii</sup>, O22<sup>iv</sup> and O61 (Fig. 3). Hence, the two water H atoms and the hydrogensulfate H atom could be disordered among these three contacts; however, we believe that the water molecule acts as hydrogen-bond acceptor from O61 and as hydrogen-bond donor to O12<sup>ii</sup> and O22<sup>iv</sup> (symmetry codes as in Fig. 3).

Several structures (Wickleder, 1998*a,b*, 1999, 2000) of acidic rare-earth sulfates have been described since the first structure of a lanthanide hydrogensulfate,  $\text{Gd}(\text{HSO}_4)_3$  (Hummel *et al.*,



**Figure 4**

The packing of the title compound, with the water molecules shown as dark spheres (red in the electronic version of the paper) and the potassium ions shown as light-grey spheres. (a) View along the *b*-axis direction; the structure consists of  $[\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^{5-}$  monomers, discrete hydrogensulfate groups, potassium ions and water molecules. (b) View along the *c*-axis direction; there are two types of alternating layers, parallel to the *ac* plane, with compositions  $[\text{K}_4\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^-$  and  $[\text{K}_2(\text{HSO}_4)(\text{H}_2\text{O})]^+$ .

1994), was published. These structures are built up by eight- or nine-coordinate rare-earth ions held together by sulfate groups, bridging by corner sharing. The structure of the title compound is essentially different from these structures; it is an acidic ternary sulfate, containing a second cation. This is unique, as the structure contains a rare-earth monomer,  $[\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^{5-}$ . Usually, rare-earth sulfates form layers or three-dimensional networks mediated by bridging sulfate groups. Only one structure has been described, *viz.*  $(\text{NH}_4)_8[\text{Ce}_2(\text{SO}_4)_8] \cdot 4\text{H}_2\text{O}$  (Shan & Huang, 1998), containing distinct rare-earth dimers,  $[\text{Ce}_2(\text{SO}_4)_8]^{8-}$ . The packing of the title compound is shown in Fig. 4. The  $[\text{Ce}(\text{HSO}_4)(\text{SO}_4)_4]^{5-}$  monomers, water molecules, hydrogensulfate groups and potassium ions are held together mainly by ionic interactions.

## Experimental

$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  (1.5 g, 3.75 mmol) was dissolved in water (10 ml) and  $\text{Ce}(\text{OH})_4$  was precipitated with ammonia (15 M). Sulfuric acid (9 M) was added to a 1:2 molar mixture of  $\text{Ce}(\text{OH})_4$  and  $\text{K}_2\text{CrO}_4$  until the solid residue was completely dissolved. An equal volume of a saturated aqueous solution of  $\text{K}_2\text{CrO}_4$  was then added to the sample. Light-yellow crystals, shaped as square plates, started to form after a few weeks.

### Crystal data

$\text{K}_6[\text{Ce}(\text{HSO}_4)_2(\text{SO}_4)_4] \cdot \text{H}_2\text{O}$	$V = 2510.75 (8) \text{ \AA}^3$
$M_r = 969.10$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.2377 (2) \text{ \AA}$	$\mu = 3.41 \text{ mm}^{-1}$
$b = 19.8722 (4) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 11.2430 (2) \text{ \AA}$	$0.36 \times 0.36 \times 0.07 \text{ mm}$
$\beta = 90.142 (1)^\circ$	

### Data collection

Bruker SMART CCD area-detector diffractometer	43581 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	8933 independent reflections
$T_{\min} = 0.373$ , $T_{\max} = 0.796$	7743 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.041$

**Table 1**

Selected bond lengths ( $\text{Å}$ ).

Ce—O53	2.363 (4)	S3—O33	1.454 (5)
Ce—O42	2.367 (4)	S3—O31	1.456 (4)
Ce—O34	2.367 (4)	S3—O34	1.497 (4)
Ce—O24	2.384 (4)	S3—O32	1.531 (4)
Ce—O22	2.430 (4)	S4—O41	1.447 (4)
Ce—O14	2.433 (3)	S4—O44	1.465 (5)
Ce—O32	2.435 (4)	S4—O43	1.503 (4)
Ce—O43	2.439 (4)	S4—O42	1.538 (4)
Ce—O52	2.443 (4)	S5—O51	1.444 (4)
S1—O11	1.404 (5)	S5—O54	1.461 (5)
S1—O13	1.450 (4)	S5—O53	1.502 (4)
S1—O14	1.466 (3)	S5—O52	1.522 (4)
S1—O12	1.478 (5)	S6—O62	1.465 (7)
S2—O21	1.447 (4)	S6—O63	1.478 (6)
S2—O23	1.458 (5)	S6—O64	1.481 (6)
S2—O22	1.507 (4)	S6—O61	1.525 (6)
S2—O24	1.538 (4)		

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	353 parameters
$wR(F^2) = 0.089$	H-atom parameters not defined
$S = 1.01$	$\Delta\rho_{\text{max}} = 1.68 \text{ e \AA}^{-3}$
8933 reflections	$\Delta\rho_{\text{min}} = -0.74 \text{ e \AA}^{-3}$

H atoms were not located. The crystal under investigation was twinned, mimicking tetragonal symmetry because of the similarity between the  $a$  and  $c$  parameters and the closeness of the  $\beta$  angle to  $90^\circ$  [twin law (001, 010,  $\bar{1}00$ )]. The twin volume ratio was refined to 0.537 (1):0.463 (1). The highest difference peak is located close (0.67  $\text{Å}$ ) to atom K6A.

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, 2003); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: SHELXTL.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3068). Services for accessing these data are described at the back of the journal.

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