Potassium cerium(III) bis(sulfate) monohydrate, $KCe(SO_4)_2 \cdot H_2O$

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The crystal structure of potassium cerium(III) bis(sulfate) monohydrate, $KCe(SO_4)_2 \cdot H_2O$, is built up from irregular independent SO_4 tetrahedra, CeO_9 polyhedra in the form of distorted tricapped trigonal prisms and K^+ ions. Hydrogen bonding between the free water molecule and sulfate groups supplement the ionic bonds characteristic of the rest of the structure.

Comment

Recently, there has been a great deal of interest in rare earth complexes because of their important physical properties, including magnetism and luminescence (Wegh *et al.*, 2000). Luminescence studies of Ce-doped compounds have demonstrated the fact that trivalent cerium ions give a better performance than all other rare earth ions (Nair *et al.*, 2000). Cerium gives a different thermostimulated luminescence peak
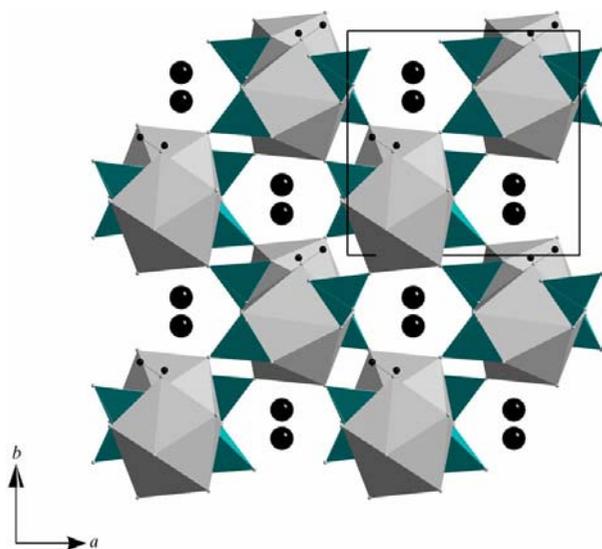
structure, probably related to the Ce^{3+}–Ce^{2+} redox mechanism. In previous studies (Guillou *et al.*, 1993; Audebrand *et al.*, 1998), it was shown that those trivalent cerium compounds could be obtained from a solution of hydrated Ce^{IV} sulfate or oxide in nitric acid. An alternative synthesis of a new compound under safer conditions (approximately neutral pH) was encountered while investigating the system $Ce(SO_4)_2 \cdot H_2O$–$KSCN$–H_2O. The high oxidation power of the Ce^{IV} ion towards the thiocyanate group leads to the formation of a new compound, shown here to be potassium cerium(III) bis(sulfate) monohydrate, $KCe(SO_4)_2 \cdot H_2O$.

The structure of the title compound comprises CeO_9 polyhedra and SO_4 tetrahedra, which are linked by common edges and vertices forming a semi-infinite three-dimensional network. K^+ ions occur in structural channels along [010] (Fig. 1).

The coordination environments of the rare earth ions consist of nine O atoms in a configuration best described as an irregular tricapped trigonal prism (Fig. 2*a*). The nine O atoms are associated with one water molecule and six sulfate groups, two of which share common edges with the CeO_9 polyhedra. Each sulfate group bridges three Ce polyhedra (Fig. 3). The Ce—O bond lengths, ranging from 2.432 (3) to 2.699 (4) Å (Table 1), are similar to the analogous distances found in $NaCe(SO_4)_2 \cdot H_2O$ (Blackburn & Gerkin, 1995) and $RbCe(SO_4)_2 \cdot H_2O$ (Robinson & Jasty, 1998). The mean Ce—O distance (2.549 Å) is also in good agreement with the value (2.53 Å) calculated by the bond-valence sum method (Brown, 1981) for Ce^{III} bonded to nine O atoms.

The ninefold configuration of Ce^{III} in $KCe(SO_4)_2 \cdot H_2O$ is typical of the majority of monohydrated alkali metal rare

Figure 1
A projection of the structure of $KCe(SO_4)_2 \cdot H_2O$ along the *c* axis. Large circles represent K atoms.
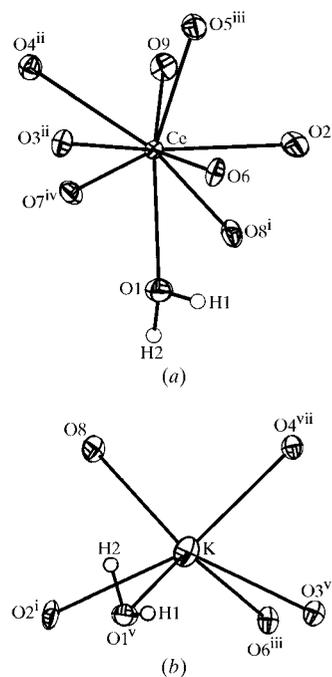

Figure 2
A view of the environment of (*a*) the Ce atom and (*b*) the K atom, showing the atom-numbering scheme. The symmetry codes are as in Table 1.

earth sulfate complexes and of rare earth ions in general. For early members of this particular rare earth series, the anionic part of the structure around the rare earth ions is relatively stable, with a coordination number of nine for Ce, Pr, La and Nd (Blackburn & Gerkin, 1994, 1995; Iskhakova *et al.*, 1985, 1988). For later members of this sulfate series, such as Gd (Sarukhanyan *et al.*, 1984), the coordination number decreases to eight, presumably in association with the lanthanide contraction. The rare earth configuration also varies slightly for hydrated alkali metal rare earth chloride complexes involving organic cations on the anionic structure (Mackenstedt & Urland, 1994). The change of the coordination number from nine in the heptahydrates to eight in the hexahydrates of the rare earth chlorides is also relevant (Kepert *et al.*, 1994). Furthermore, the coordination number decreases from nine (in the case of La; Reuter & Frenzen, 1994) to eight (in the case of Ce–Tb; Reuter *et al.*, 1994) for the trihydrates of these chlorides.

The two crystallographically inequivalent S atoms are each surrounded by four O atoms, establishing sulfate anions that are without symmetry constraints and which consequently form slightly irregular tetrahedra. The S1- and S2-centered sulfate tetrahedra stack in planes normal to [100], which alternate with respect to each other (Fig. 4). In their tetrahedra, both S1 and S2 form two short, one medium and one long S—O bond, which are in the ranges 1.459 (4)–1.479 (4) and 1.465 (4)–1.479 (3) Å, respectively. The O—S—O bond angles are consistent with slightly distorted tetrahedra [106.8 (3)–111.6 (2) and 105.9 (3)–111.6 (2)°, respectively, for the S1 and S2 tetrahedra (Table 1)]. Furthermore, the smallest O—S—O angle for both the S1 and the S2 tetrahedra corresponds to the O–O edges shared with the CeO_9 polyhedra.

The K^+ cations are surrounded by six O atoms, including one water O atom (Fig. 2*b*). These atoms form an irregular KO_6 triangular prism; in fact, the K—O distances range from
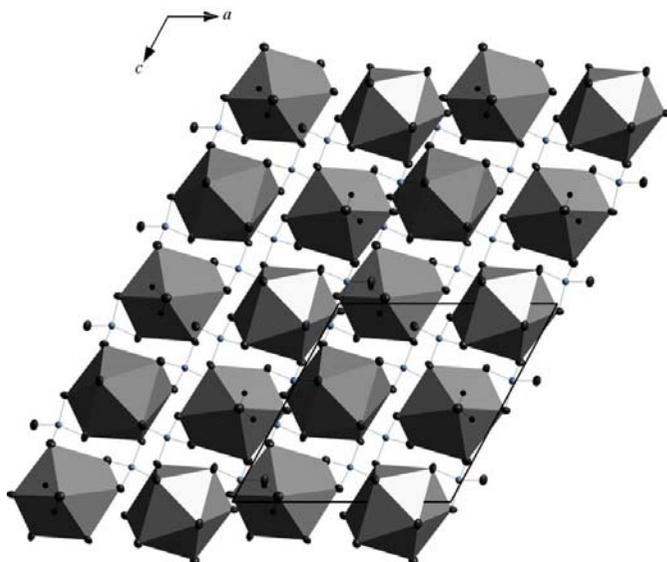

Figure 3
A projection of the structure of $KCe(SO_4)_2\cdot H_2O$ along the *b* axis.

Figure 4
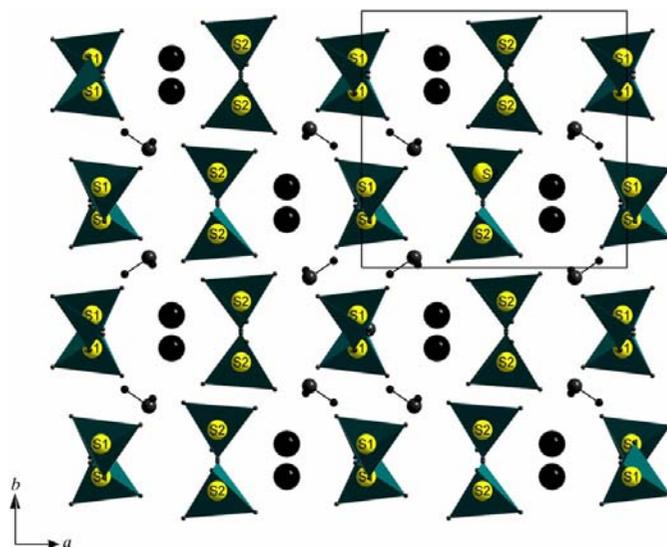A projection of the structure of $KCe(SO_4)_2\cdot H_2O$ along the *c* axis. CeO_9 polyhedra have been omitted.

2.805 (3) to 2.981 (5) Å (Table 1). In the analogous compound $LiCe(SO_4)_2\cdot H_2O$ (Iskhakova *et al.*, 1987), the monovalent cation, with coordination number four, forms LiO_4 tetrahedra. The reduction in radii between the K^+ and Li^+ ions is associated with a structural phase change from the compact three-dimensional framework of the present $KCe(SO_4)_2\cdot H_2O$ structure to the layered structure of $LiCe(SO_4)_2\cdot H_2O$.

In contrast to other structural analogues, the water molecule of $KCe(SO_4)_2\cdot H_2O$ appears to be well ordered, being characterized by an O atom whose displacement parameters are consistent with those of other well ordered atoms in the structure. For the $NaCe(SO_4)_2\cdot H_2O$, $NaLa(SO_4)_2\cdot H_2O$ (Blackburn & Gerkin, 1994, 1995) and $AgCe(SO_4)_2\cdot H_2O$ (Audebrand *et al.*, 1998) analogues, the water O atom was better modeled as disordered equally over two sites.

According to the classical geometry of hydrogen bonds, water molecules are linked to sulfate anions by O—H···O hydrogen bonds (Table 2). Each sulfate tetrahedron establishes one hydrogen bond with a water molecule *via* the O atom corresponding to the longer S—O bonds, namely atoms O4 and O7, respectively, for the S2 and S1 tetrahedra. O—H···O hydrogen bonds act in the same way as the ionic contacts to provide connectivity between the cerium polyhedra and the sulfate anions, thereby improving the stability of the structure.

Experimental

Crystals of the title compound were synthesized at room temperature by mixing aqueous solutions of $Ce(SO_4)_2\cdot 4H_2O$ and KSCN until the yellow color was no longer detected. The colorless solution was allowed to evaporate at room temperature and colorless crystals of $KCe(SO_4)_2\cdot H_2O$ had formed within a few days. The compound was characterized by elemental chemical analysis and thermogravimetric studies to determine the formula, which was later confirmed by refinement of the crystal structure.

Crystal data

$KCe(SO_4)_2 \cdot H_2O$
$M_r = 389.3$
Monoclinic, $P2_1/c$
$a = 10.1163$ (2) Å
$b = 8.588$ (4) Å
$c = 10.3823$ (6) Å
$\beta = 118.39$ (3)°
$V = 793.5$ (4) Å^3
$Z = 4$

$D_x = 3.258$ (2) Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3322 reflections
$\theta = 2.0$–27.0°
$\mu = 6.81$ mm^{-1}
$T = 293$ K
Needle, colorless
$0.1 \times 0.05 \times 0.03$ mm

Data collection

Oxford Instruments Xcalibur point-detector diffractometer
$\theta/2\theta$ scans
Absorption correction: Gaussian (*JANA2000*; Petricek & Dusek, 2000)
$T_{min} = 0.483$, $T_{max} = 0.595$
3334 measured reflections

1729 independent reflections
1267 reflections with $I > 3\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.0°$
$h = -12 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.055$
$S = 1.18$
1729 reflections
127 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(I) + 0.0004I^2]$

$(\Delta/\sigma)_{max} = 0.015$
$\Delta\rho_{max} = 1.40$ e Å^{-3}
$\Delta\rho_{min} = -1.71$ e Å^{-3}
Extinction correction: B-C type 1 Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 0.064491

Table 1
Selected interatomic distances (Å).

Ce1—O1	2.595 (4)	K1—O8	2.805 (3)
Ce1—O2^i	2.578 (5)	S1—O2	1.475 (3)
Ce1—O3^{ii}	2.508 (4)	S1—O7	1.479 (4)
Ce1—O4^{ii}	2.671 (4)	S1—O8	1.469 (3)
Ce1—O5^{iii}	2.449 (3)	S1—O9	1.459 (4)
Ce1—O6	2.496 (3)	S2—O3	1.475 (4)
Ce1—O7^{iv}	2.514 (2)	S2—O4	1.479 (3)
Ce1—O8^i	2.699 (4)	S2—O5	1.468 (4)
Ce1—O9	2.432 (3)	S2—O6	1.465 (4)
K1—O1^v	2.981 (5)	O1—O4	2.929 (5)
K1—O2^i	2.897 (3)	O1—O7^{viii}	2.852 (4)
K1—O3^{vi}	2.812 (3)	O1—H1	0.82 (8)
K1—O4^{vii}	2.960 (4)	O1—H2	0.98 (7)
K1—O6^{iii}	2.845 (4)		

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (v) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $1-x, 1-y, 2-z$; (vii) $x, 1+y, z$; (viii) $x, y-1, z$.

All H atoms were located in difference Fourier maps and were refined isotropically (see Table 1).

Data collection: *KM4B8* (Galdecki *et al.*, 1996); cell refinement: *KM4B8*; data reduction: *JANA2000* (Petricek & Dusek, 2000);

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O4	0.82 (5)	2.16 (7)	2.929 (5)	156 (6)
O1—H2$\cdots$O7^{viii}	0.98 (7)	1.90 (7)	2.852 (4)	163 (9)

Symmetry code: (viii) $x, y-1, z$.

program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *JANA2000*; molecular graphics: *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *JANA2000*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1048). Services for accessing these data are described at the back of the journal.

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