

1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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(NH₄)₈[Ce₂(SO₄)₈].4H₂O

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Abstract

Crystals of the title compound, octaammonium dicerium octasulfate tetrahydrate, suitable for X-ray work, were prepared by a hydrothermal reaction. The structure is made up of [Ce₂(SO₄)₈]⁸⁻ anions, interacting with the crystallization waters and the NH₄⁺ cations through hydrogen bonds. The Ce^{IV} atom in the [Ce₂(SO₄)₈]⁸⁻ anion is ninefold coordinated by O atoms belonging to sulfate groups. The coordination polyhedron is a somewhat distorted tricapped trigonal prism. The Ce—O distances range from 2.325 (2) to 2.478 (2) Å.

Comment

Sulfates containing cerium(IV) are widely used as oxidants in quantitative analysis and organic chemical synthesis (Toshima & Yan, 1995). Several structures of cerium(IV) sulfates have been investigated by Lindgren (1976, 1977*a,b*) in the seventies. Barnes (Barnes, 1995; Barnes *et al.*, 1993) reported the structures of an acid terbium(III) cerium(IV) sulfate hydrate and an acid neodymium(III) cerium(IV) sulfate hydrate. These structures extend through sulfate bridges to form infinite strings, layers and three-dimensional networks. They contain Ce^{IV} ions coordinated by eight or nine O atoms. The coordination polyhedra are of different kinds, *e.g.* square antiprism, dodecahedron or tricapped trigonal prismatic coordination. In this paper, we report the structure of a new dimeric ammonium cerium(IV) sulfate hydrate. Because cerium(IV) sulfates strongly hydrolyze in aqueous solution, it is difficult to obtain crystals of such compounds under normal conditions. The hydrothermal method was employed to grow single crystals of the title compound.

The dimeric anion, [Ce₂(SO₄)₈]⁸⁻, is a distinct chemical unit in the structure. The structure of this anion is shown in Fig. 1. First of all, two sulfate anions act as the bridging groups between the two Ce^{IV} ions. The other sulfate anions all act as bidentate terminal ligands. Each Ce^{IV} is nine-coordinated, with six O atoms forming a trigonal prism (top face: O13, O8 and O5; bottom face: O11, O4 and O15). The three rectangular faces are each capped by an O atom [O9ⁱ, O10 and O3; symmetry code: (i) 1 - x, -y, -z]. All O atoms coordinated to the Ce^{IV} centers are from the sulfate groups. The nine Ce—O bond lengths range from 2.325 (2) to 2.478 (2) Å. The O—Ce—O angles, ranging from 56.86 (8) to 156.44 (9)°, are in agreement with those found in similar compounds (Barnes *et al.*, 1993;

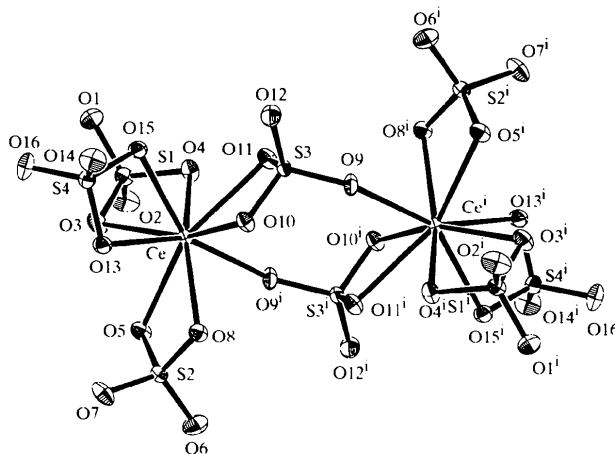


Fig. 1. An ORTEP (Johnson, 1965) representation of the title anion, showing 35% probability displacement ellipsoids and the atom-numbering scheme. The symmetry code is as given in Table 1.

Barnes, 1995). Other selected bond distances and angles are given in Table 1. The structural characterization of the water molecules was also of interest, since in the title compound the water O atoms are not coordinated to the metal ions, contrary to the earlier results for similar compounds containing Ce^{IV} . In the present structure, the unit cell contains eight water molecules and 16 NH_4^+ ions, which form hydrogen bonds stabilizing the structure. The hydrogen bonding in this compound involves water O atoms, ammonium N atoms and the terminal O atoms in the sulfate groups as acceptors, *e.g.* O16—O17 = 2.851 (4), O14—N3 = 2.849 (4) and O6—O18 = 2.796 (5) Å.

Experimental

Commercially available $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ (800 mg) was sealed in a thick-walled Pyrex tube (~25 cm long) with 0.3 ml distilled water. The tube was heated at 383 K for 5 d to afford bright yellow crystals of the title compound in about 30% yield.

Crystal data

$(\text{NH}_4)_8[\text{Ce}_2(\text{SO}_4)_8] \cdot 4\text{H}_2\text{O}$
 $M_r = 1265.07$
 Monoclinic
 $P2_1/c$
 $a = 12.6472$ (7) Å
 $b = 11.3613$ (6) Å
 $c = 13.6908$ (7) Å
 $\beta = 110.363$ (1)°
 $V = 1844.3$ (2) Å³
 $Z = 2$
 $D_x = 2.278$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.7107$ Å
 Cell parameters from 7759 reflections
 $\theta = 1.59$ – 27.11 °
 $\mu = 3.015$ mm⁻¹
 $T = 296$ (1) K
 Octahedral
 $0.20 \times 0.20 \times 0.15$ mm
 Yellow

Data collection

Quantum CCD diffractometer
 ω scans
 Absorption correction: empirical *via* simulated ψ scans (SADABS; Sheldrick, 1997)
 $T_{\min} = 0.564$, $T_{\max} = 0.636$
 9837 measured reflections

3874 independent reflections
 3179 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$
 $\theta_{\max} = 27.11$ °
 $h = -14 \rightarrow 15$
 $k = -14 \rightarrow 8$
 $l = -17 \rightarrow 15$
 Intensity decay: none

Refinement

Refinement on F
 $R = 0.022$
 $wR = 0.034$
 $S = 0.973$
 3179 reflections
 245 parameters
 H atoms not located
 $w = 1/[\sigma^2(F_o) + 0.00078|F_o|^2]$
 $(\Delta/\sigma)_{\max} = 0.011$

$\Delta\rho_{\max} = 0.72$ e Å⁻³
 $\Delta\rho_{\min} = -0.45$ e Å⁻³
 Extinction correction: Zachariasen (1967)
 Extinction coefficient: 3.2 (4) $\times 10^{-7}$
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ce—O3	2.397 (2)	S1—O1	1.440 (3)
Ce—O4	2.388 (2)	S1—O2	1.439 (3)
Ce—O5	2.386 (2)	S1—O3	1.517 (3)
Ce—O8	2.435 (2)	S1—O4	1.514 (2)
Ce—O9'	2.325 (2)	S3—O9	1.491 (2)
Ce—O10	2.416 (2)	S3—O10	1.496 (2)
Ce—O11	2.478 (2)	S3—O11	1.485 (2)
Ce—O13	2.368 (2)	S3—O12	1.435 (3)
Ce—O15	2.368 (2)		
O3—Ce—O5	66.92 (9)	O9'—Ce—O10	92.28 (9)
O3—Ce—O8	120.39 (8)	O9'—Ce—O13	151.28 (9)
O3—Ce—O9'	111.71 (9)	O10—Ce—O11	56.86 (8)
O3—Ce—O13	79.99 (9)	O10—Ce—O13	81.91 (9)
O4—Ce—O5	107.08 (9)	O11—Ce—O13	121.78 (9)
O4—Ce—O8	156.44 (9)	O9—S3—O10	108.7 (1)
O4—Ce—O13	126.37 (9)	O9—S3—O11	109.5 (2)
O5—Ce—O15	130.93 (9)	O9—S3—O12	110.0 (2)
O8—Ce—O10	69.27 (8)	O10—S3—O11	102.8 (1)
O8—Ce—O11	118.60 (8)	O10—S3—O12	112.2 (2)
O8—Ce—O15	124.19 (9)	O11—S3—O12	113.4 (2)

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

Because the electron-density maps were dominated by the Ce atoms, the H atoms could not be directly located from the difference Fourier maps. No effort was made to calculate their positions.

Data collection: SMART (Siemens, 1995). Cell refinement: SAINT (Siemens, 1995). Data reduction: SAINT. Program(s) used to solve structure: SIR92 (Altomare *et al.*, 1993). Program(s) used to refine structure: TEXSAN (Molecular Structure Corporation, 1997). Software used to prepare material for publication: TEXSAN.

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