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The Crystal Structure of Hydrogen Cerium(III) Sulfate Hydrate, $[H_3O][Ce(SO_4)_2] \cdot H_2O$

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$[H_3O][Ce(SO_4)_2] \cdot H_2O$ crystallizes in the monoclinic system with unit-cell dimensions (from single-crystal data) $a = 9.359(4)$, $b = 9.926(4)$, $c = 8.444(3)$ Å, $\beta = 96.53(9)°$ and space group $P2_1/n$, $z = 4$. The structure was solved by conventional heavy-atom methods using 1787 counter-measured reflections (Mo$K\alpha$ radiation), and refined using full-matrix least-squares techniques to an R of 0.0465 ($\omega R = 0.0413$). The structure consists of cerium(III) ions in irregular nine-coordination to oxygen atoms from two bidentate sulfate ions, four monodentate sulfate oxygen atoms, and one water molecule. The oxonium ions are present as isolated ions in the structure and take part in the hydrogen bonding network. The Ce-O bond lengths range from 2.454(7) to 2.626(6) Å.

Introduction

Structural studies of a variety of hydrated cerium(III) and cerium(IV) sulfates have shown that the coordination sphere about the cerium ion reflects the oxidation state of the ion (see Table I and references therein). Cerium(IV) sulfates characteristically contain cerium in eightfold coordination, while cerium(III) sulfates contain cerium in nine-coordinate sites.

During attempts to prepare hydrated cerium(III) sulfates, crystals were produced that did not correspond to those of previously reported hydrates. The compound proved to be the oxonium salt of $[Ce(SO_4)_2]^-$. The single-crystal structure determination of this material is reported here.

Experimental

Colorless bipyramidal monoclinic crystals were obtained by dissolving cerium(III) oxalate in hot concentrated sulfuric acid, decanting the supernatant liquid and, after allowing it to cool, standing it for several weeks in a dessicator containing dry silica gel.

A single bipyramidal crystal of dimensions 0.16 × 0.06 × 0.05 mm was selected using a polarizing microscope and mounted with clear epoxy resin ("Resiweld 5") on a silica capillary. The crystal data below were obtained using a Philips PW1100 computer-controlled single-crystal diffractometer in a manner described previously (*1*).

Crystal data: $[H_3O]$ $[Ce(SO_4)_2] \cdot H_2O$, $M = 369.27$, $a = 359(4)$, $b = 9.926(4)$, $c = 8.444(3)$ Å, $\beta = 96.53(9)°$, $U = 779.3$ Å^3, $D_c = 3.15$ g cm^{-3}, $z = 4$, $D_m = 3.12(3)$ g cm^{-3} (flotation, CH_2I_2 and CCl_4). $F(000) = 700$, $\mu = 60.3$ cm^{-1} for Mo$K\alpha$ radiation (λ =

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TABLE I

COORDINATION NUMBERS AND Ce–O DISTANCES FOR CERIUM(III) AND CERIUM(IV) SULFATES

Compound	Coordination number	Mean Ce–O (Å)	Range of Ce–O (Å)	Ref.
$[H_2O]\ [Ce(SO_4)_2] \cdot H_2O$	9	2.538	2.454(7)–2.626(6)	
$Ce_2(SO_4)_3 \cdot 4H_2O$	9	2.59	2.22(9)–3.10(11)	(*6*)
$Ce_2(SO_4)_3 \cdot 5H_2O$	9	six 2.39–2.55 plus[a]	2.57, 2.59, 2.82[b]	(*7*)
$Ce_2(SO_4) \cdot 9H_2O$	9, 12	2.513, 2.708	2.507–2.823[b]	(*8*)
$NaCe(SO_4)_2 \cdot H_2O$	9	2.534	2.477(10)–2.584(10)	(*9*)
$Ce(SO_4)_2$	8	2.23	2.07(4)–2.38(4)	(*10*)
$Ce(SO_4)_2 \cdot 4H_2O$	8	2.36	2.292(6)–2.388(9)	(*11*)
$CeO(SO_4) \cdot H_2O$	8	2.364	2.188(3)–2.587(4)	(*12*)
$Ce_2(OH)_2(SO_4)_3 \cdot 4H_2O$	8	2.328	2.223(7)–2.406(9)	(*13*)
$Ce_6O_4(OH)_4(SO_4)_6$	8	2.34	2.22–2.39[b]	(*14*)

[a] Details not given.

[b] Estimated SDs not given.

0.7107 Å). Space group $P2_1/n$ from systematic absences $0k0, k$ odd and $h0l, h + l$ odd. This alternative setting of $P2_1/c$ (C_{2h}^5, N° 14) was chosen for convenience as β is then closer to 90°.

Intensity Measurements

Intensity measurements were made with the crystal described above using the Philips PW1100 diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite crystal. Three thousand fifty-nine reflections were measured using the θ–2θ scan technique within the range $3° < \theta < 30°$ with a symmetric scan range of $\pm 0.55°$ in 2θ from the calculated Bragg angle (with an allowance for dispersion) at a scan rate of 0.05° sec^{-1}. No reflection was sufficiently strong to warrant the insertion of an attenuation filter. Of the 3759 reflections measured, 1787 were considered to be significantly above background ($I \geq 3\sigma\ (I)$) and only these were used during the refinement. Three standard reflections measured at 2-hr intervals showed no significant variation in intensity.

The data were reduced in a manner described previously (*1*) and were corrected for absorption on the basis of indexed crystal faces ($1\ 1\ \bar{1}$, $\bar{1}\ \bar{1}\ 1$, $\bar{1}\ 1\ 1$, $1\ \bar{1}\ \bar{1}$, $\bar{1}\ 2\ \bar{1}$, $1\ \bar{2}\ 1$, $1\ 2\ 1$, and $\bar{1}\ \bar{2}\ \bar{1}$) using the program SHELX-76 (*2*). Maximum and minimum transmission factors were 0.6314 and 0.4982, respectively. The atomic scattering factors used were for Ce°, S°, O°, and H°, corrected for anomalous dispersion, from Ref. (*3*). All calculations were carried out on the Monash University Burroughs B6700 computer; the major programs used were SHELX-76 (*2*), ORFFE (*4*), and ORTEP (*5*).

Structure Solution and Refinement

The structure was solved by Patterson methods for the cerium atom position and the oxygen and sulfur atoms were located in the subsequent difference Fourier synthesis. Full-matrix least-squares refinement of positional and isotropic thermal parameters followed by several cycles in which all atoms were refined with anisotropic thermal parameters using individual reflection weights $[\sigma(F)]^{-2}$ resulted in final values of R of 0.0465 and ωR 0.0413. [$R = \Sigma\Delta/\Sigma|F_o|$, $\omega R = [\Sigma\omega\Delta^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}}$, where $\Delta = |\ |F_o| - |F_c|\ |$]. In the final cycle of refinement

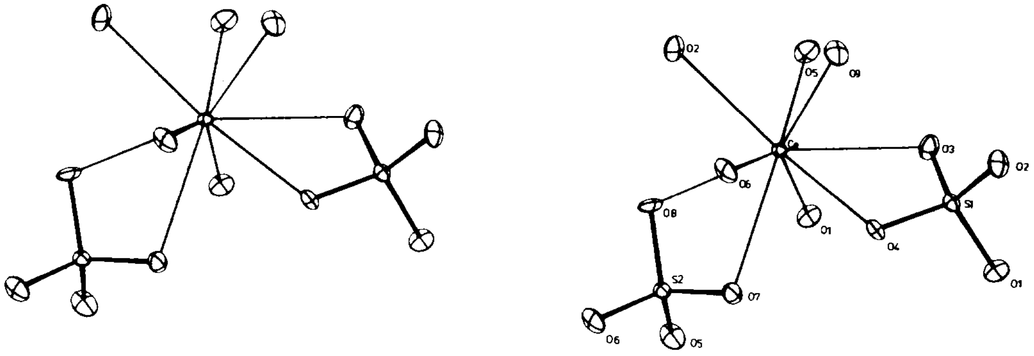

FIG. 1. A stereoscopic view of the cerium(III) coordination in $[H_3O][Ce(SO_4)_2] \cdot H_2O$ together with the numbering scheme used.

no parameter shift exceeded 1% of the estimated SD in that parameter. Final parameters with their estimated standard deviations in parentheses are presented in Table II.[1]

Structure Description and Discussion

The structure consists of cerium(III) ions in irregular (very approximately tricapped trigonal prismatic) coordination to eight oxygens of sulfate ions and one from a water molecule (Fig. 1). Sulfate ions link the cerium ions thus forming a three-dimensional array within which are sites for the hydrated hydrogen ions (Fig. 2). The Ce–O bond lengths range from 2.454(7) to 2.626(6) Å with a mean of 2.538 Å. A number of cerium(III) and cerium(IV) sulfate compounds are listed in Table I and it can be seen that Ce–O bond lengths for Ce(III)

TABLE II

FINAL ATOMIC PARAMETERS[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	2512(1)[b]	6605(1)	4678(1)	63(2)	68(2)	63(2)	−5(2)	8(1)	6(2)
S(1)	5200(2)	5883(2)	7244(3)	71(8)	104(9)	92(9)	−18(7)	7(7)	−8(8)
S(2)	731(2)	4073(2)	3153(3)	73(8)	84(9)	99(9)	−3(7)	16(7)	−16(8)
O(1)	6157(7)	4704(7)	7222(8)	13(3)	16(3)	19(4)	6(3)	5(3)	−5(3)
O(2)	598(6)	8323(8)	3697(7)	14(3)	23(3)	10(3)	0(3)	−2(2)	6(3)
O(3)	5214(6)	6730(7)	5805(7)	13(3)	21(3)	13(3)	1(3)	−2(2)	6(3)
O(4)	3675(7)	5415(6)	7203(8)	11(3)	13(3)	16(3)	−5(2)	−2(2)	−1(3)
O(5)	3625(7)	8196(7)	2963(9)	14(3)	22(4)	24(4)	1(3)	8(3)	12(3)
O(6)	−720(6)	3571(7)	3356(8)	11(3)	21(4)	19(3)	−7(3)	6(2)	−2(3)
O(7)	1638(7)	4138(7)	4695(7)	16(3)	16(3)	11(3)	−5(3)	−5(3)	4(3)
O(8)	9358(7)	4513(6)	7482(8)	17(3)	7(3)	22(4)	3(2)	1(3)	7(3)
O(9)	2057(7)	3460(8)	8373(8)	18(3)	19(3)	22(3)	0(3)	−1(3)	12(3)
O(10)	7708(9)	3573(10)	10136(10)	40(5)	43(5)	33(5)	2(4)	0(4)	−7(4)

[a] The form of the thermal ellipsoids is $\exp[-2\pi^2 (U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$.

[b] Estimated standard deviations in parentheses. Parameters × 10^4, oxygen thermal parameters × 10^3.

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[1] For a table of observed and calculated structure factors see NAPS document No. 03768 for 10 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only for each NAPS Accession Number. Institutions may use purchase orders when ordering; however, there is a billing charge for this service. Make checks payable to Microfiche Publications. Photocopies are $5.00. Microfiche are $3.00. Outside of the U.S. and Canada, postage is $3.00 for a photocopy or $1.50 for a fiche.

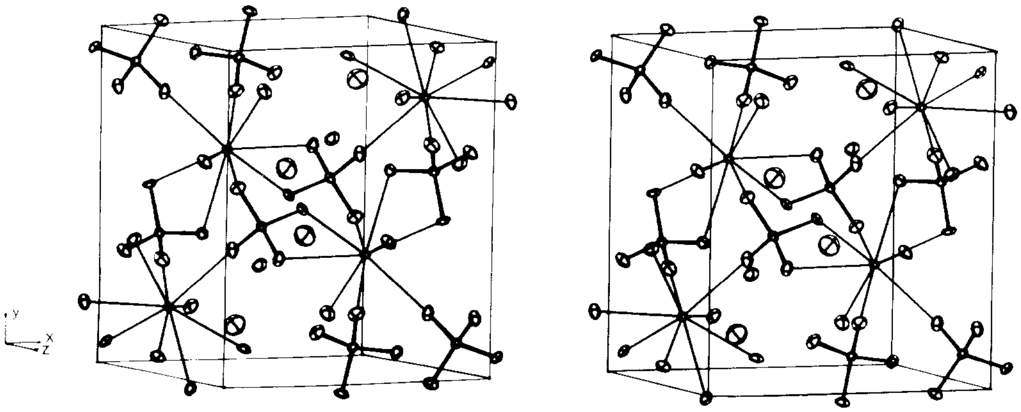

FIG. 2. A packing diagram for $[H_3O]$ $[Ce(SO_4)_2] \cdot H_2O$ in which the bidentate–monodentate bridging sulfate groups may be seen. The four larger isolated ellipsoids represent the H_3O^+ positions.

are generally >2.5 Å, while Ce(IV)–O lengths are generally <2.4 Å. The presence of cerium(III) in $[H_3O]$ $[Ce(SO_4)_2] \cdot H_2O$ was confirmed by EPR spectroscopic examination.

There are two modes of coordination of the sulfate ion to cerium; two sulfate ions are bidentate and four are monodentate ligands. The Ce–O bonds of the bidentate sulfates are significantly longer (2.568–2.626 Å, mean 2.594 Å) than the Ce–O bonds from the monodentate sulfate ions (2.454–2.543 Å, mean 2.494 Å). The chelating angles of the sulfate ions are significantly smaller than the other tetrahedral angles about sulfur: O(3)–S(1)–O(4), 104.8(4)°; O(7)–S(2)–O(8), 106.1(4)°; compared with the range of angles about sulfur of 104.8–112.3, mean 109.5°.

The oxonium ion (O(10)) has five oxygens at distances between 2.85 and 2.94 Å from it and three at slightly greater distances, O(8) at 3.01(1) Å, O(9) at 3.20(1) Å, and O(5) at 3.28(1) Å, making eight neighbors in all. The six shorter distances are typical of hydrogen bonding between water and oxygen (*15*). The water molecule (O(9)) is coordinated to cerium and is probably hydrogen bonded to O(8) (2.76(1)Å) and O(4) (2.76(1)Å). It was not possible to locate the hydrogen atoms unambiguously in this structure and any discussion of hydrogen bonding would only be speculative.

The sulfur–oxygen–cerium angles are

TABLE III

SELECTED BOND LENGTHS (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ce–O(1)	2.504(7)	S(1)–O(1)	1.476(1)
Ce–O(2)	2.543(7)	S(1)–O(2)	1.470(7)
Ce–O(3)	2.602(6)	S(1)–O(3)	1.478(7)
Ce–O(4)	2.568(6)	S(1)–O(4)	1.498(7)
Ce–O(5)	2.454(7)	S(2)–O(5)	1.463(8)
Ce–O(6)	2.496(7)	S(2)–O(6)	1.474(7)
Ce–O(7)	2.581(7)	S(2)–O(7)	1.472(6)
Ce–O(8)	2.626(6)	S(2)–O(8)	1.501(7)
Ce–O(9)	2.472(7)		
S(1)–O(1)–Ce	140.0(4)	O(10)–O(1)	2.93(1)
S(1)–O(2)–Ce	137.2(4)	O(10)–O(3)	2.85(1)
S(1)–O(3)–Ce	100.0(3)	O(10)–O(4)	2.90(1)
S(1)–O(4)–Ce	100.9(3)	O(10)–O(6)	2.94(1)
		O(10)–O(7)	2.88(1)
S(2)–O(5)–Ce	175.8(5)	O(3)–O(10)–O(7)	66.6(3)
S(2)–O(6)–Ce	142.9(4)	O(3)–O(10)–O(4)	144.9(4)
S(2)–O(7)–Ce	100.8(3)	O(3)–O(10)–O(1)	107.5(3)
S(2)–O(8)–Ce	98.1(3)	O(3)–O(10)–O(6)	88.4(3)
		O(7)–O(10)–O(4)	104.2(3)
		O(7)–O(10)–O(1)	96.8(3)
		O(7)–O(10)–O(6)	104.4(3)
		O(4)–O(10)–O(1)	107.2(3)
		O(4)–O(10)–O(6)	60.3(2)
		O(1)–O(10)–O(6)	157.4(4)

significantly smaller for the oxygens of the chelating sulfate groups (< 100.9°) than for the unidentate sulfate groups (> 137.2°, < 175.8°). The S(2)–O(5)–Ce angle of 175.8° is perhaps surprisingly large; however, it is associated with the shortest Ce–O bond distance (2.454(7)Å), and the shortest S–O distance (1.463(8)Å). The S–O–Ce angle appears to limit the oxygen–cerium approach distance, leading to lengthening of the Ce–O contacts for the chelating oxygens compared with the Ce–O distances for nonchelating oxygen. The angular constraint imposed by the oxygen atoms is to some extent accommodated by a decrease in the chelating angle at the sulfur atom.

The structure of $[H_3O]\,[Ce(SO_4)_2] \cdot H_2O$ is, in many respects, similar to that of $NaCe(SO_4)_2 \cdot H_2O$, although the sodium salt crystallizes in space group $P3_121$ and the cerium ion lies on a twofold axis thus conferring symmetry on the cerium(III) polyhedron. The coordination sphere of H_3O^+ is similar to that of Na^+ in the sodium salt in that there are six oxygens at 2.44(1) to 2.54(1)Å and two longer contacts at 2.87(1)Å. The mean Na–O distance is 2.58 Å compared with 3.00 Å for the mean H_3O^+–O distance. The greater volume per molecule for the acid salt compared with the sodium salt arises probably from the additional hydrogen bonding involved in the acid salt structure, rather than from the differences between the volume occupied by Na^+ compared with H_3O^+.

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