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The Crystal Structure of Sodium Cerium(III) Sulfate Hydrate, $NaCe(SO_4)_2.H_2O$

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The crystal structure of $NaCe(SO_4)_2.H_2O$ has been determined from three-dimensional X-ray diffractometer data. The crystals are trigonal, space group $P3_121$, with $a=7.0134(14)$ Å, $c=12.920(3)$ Å and $Z=3$. The positions of the non-hydrogen atoms were evaluated from Patterson and electron density maps. Full matrix least squares refinement based on 574 reflexions yielded a final R value of 0.047.

A three-dimensional network is formed by the linking of cerium atoms and sulfate groups. The voids that remain are occupied by sodium ions and water molecules.

Cerium is coordinated by nine oxygen atoms, one water molecule and eight sulfate oxygens.

The coordination polyhedron can be described as a pentagonal bipyramid with the axial bonds each consisting of two bonds to sulfate groups acting as bidentate ligands. The Ce—O bond distances are in the range 2.477—2.584 Å with the average 2.534 Å.

In order to study cerium(IV)—oxygen polyhedra a number of structures [1–5] of solid phases in the system $CeO_2-SO_3-H_2O$ have been determined at this Institute. Attempts have also been made to prepare mixed Ce(III)—Ce(IV) sulfates and a structure determination of such a compound is in progress.[6]

In connection with the latter project a structure investigation of the title compound, *viz.* $NaCe(SO_4)_2.H_2O$, has been undertaken.

EXPERIMENTAL

Freshly precipitated $Ce(OH)_3$ was dissolved in 0.5 M H_2SO_4 and mixed with an aqueous solution of Na_2SO_4 in approximate molar ratios 1:1. About 25 ml of the solution was transferred to a thickwalled glass tube. This was sealed and heated to 230 °C in an oven for a week. A large number of microcrystals were obtained and in addition some transparent hexagonal prisms of suitable size for single crystal investigation. A Guinier recording showed the microcrystals to be part of the same solid phase.

A crystal of approximate dimensions $0.2\times 0.2\times 0.25$ mm was mounted along **a** on a Weissenberg camera and the zero, first and second layer-lines were recorded. Reflexions of the types h,k,l; $k,h,-l$; $k,-h-k,l$; $h+k,-k,l$; $h+k,-h,-l$ and $h,-h-k,-l$ proved to have the same intensities implying that the crystal has trigonal symmetry. The only reflexions systematically absent were $00l$ for $l\neq 3n$. The space group is thus uniquely determined to be $P3_121$ (or its enantiomorph $P3_221$).

Cell constants were obtained from a Guinier diagram using monochromatized Cu$K\alpha$ radiation and $Pb(NO_3)_2$ ($a=7.8566$ Å at 21 °C) [7] as an internal standard. A least squares refinement of 12 indexed lines (program: POWDER [8]) resulted in the following lattice parameters: $a=7.0134(14)$ Å and $c=12.920(3)$ Å. Assuming $Z=3$ the calculated density $D_X=3.378$ g cm^{-3}.

The crystal chosen for the preliminary Weissenberg studies was transferred to a PAILRED single crystal diffractometer. Nine layers, $0kl-8kl$, were registered with graphite monochromatized Mo$K\alpha$ radiation. 574 reflexions were retained when an observed/unobserved cutoff at 3.0 $\sigma(I)$ was employed. The intensities were reduced to structure factors by application of Lorentz and polarisation factors but no absorption correction was made.

STRUCTURE DETERMINATION AND REFINEMENT

The coordinates of the cerium and sulfur atoms were deduced from the Patterson function. A Fourier synthesis phased from these atoms showed the positions of the other atoms. The structure was refined by the least squares

Table 1. Atomic coordinates and temperature factors for $NaCe(SO_4)_2.H_2O$. Estimated standard deviations are given in parentheses. The thermal parameters have been multiplied by 10^4 for Ce, Na and S and by 10^3 for O. The temperature factor is of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	0	0.43323(16)	1/6	102(6)	139(13)	65(3)	139(0)	−10(10)	−21(0)
Na	0.4711(14)	0	1/3	266(38)	27(40)	210(34)	27(0)	17(34)	34(0)
S	0.5592(6)	0.5470(6)	0.2542(2)	131(15)	163(15)	79(9)	165(32)	−32(24)	−9(21)
O1	0.7566(16)	0.5909(17)	0.1926(8)	15(5)	12(5)	15(4)	6(8)	5(7)	−6(7)
O2	0.3827(22)	0.5049(21)	0.1819(8)	21(6)	27(7)	15(4)	22(11)	3(9)	1(9)
O3	0.4938(18)	0.3589(21)	0.3263(7)	16(5)	27(6)	12(4)	28(9)	−5(7)	−6(8)
O4	0.6111(16)	0.7406(16)	0.3194(7)	21(5)	13(4)	8(3)	16(8)	3(6)	7(7)
O5	0	0.0674(35)	1/6	39(17)	16(16)	97(20)	16(0)	−10(23)	−21(0)

program LALS.[9] In the later cycles, anisotropic temperature factors were introduced. Weights were calculated according to the formula: $w=(30+|F_o|+0.003|F_o|^2)^{-1}$, which led to a reasonable agreement between w^{-1} and $(|F_o|-|F_c|)^2$ independent of $|F_o|$. The scattering factors for Ce, S, O and Na^+ were taken from Cromer and Waber.[10] When the shifts were considerably less than the estimated standard deviations, the R value (conventional) had converged to 0.047. A difference Fourier map showed no significant peaks, except for some fluctuations in the vicinity of the heavy atoms. The final coordinates and anisotropic thermal parameters are listed in Table 1. A listing of observed and calculated structure factors may be obtained from the author on request.

DESCRIPTION AND DISCUSSION

Coordination numbers (CN) from six to twelve have been established in lanthanoid compounds but nine and eight coordination appear most frequently. Previous studies of trivalent cerium sulfates[11,12] show CN = 9 and the preferred polyhedron seems to be a tri-capped trigonal prism, D_{3h}.

Table 2. Selected distances (Å) and angles (°) for $NaCe(SO_4)_2.H_2O$.

Ce−O1	(2×)	2.477(10)	O5−O1′	(2×)	2.914(23)
O2	(2×)	2.479(13)	O2	(2×)	2.902(19)
O3	(2×)	2.584(10)	O4	(2×)	3.050(17)
O4	(2×)	2.578(9)			
O5		2.566(24)	O1−S−O2		107.9(6)
Average:		2.534	O1−S−O3		111.1(6)
Na−O1	(2×)	2.870(11)	O1−S−O4		109.7(6)
O2	(2×)	2.536(11)	O2−S−O3		111.6(7)
O3	(2×)	2.443(14)	O2−S−O4		110.2(7)
O4	(2×)	2.468(12)	O3−S−O4		106.4(6)
S−O1		1.490(11)	Five membered ring around cerium		
O2		1.458(13)	O1−Ce−O1		75.5(5)
O3		1.488(12)	O1−Ce−O2	(2×)	73.7(4)
O4		1.480(10)	O2−Ce−O5	(2×)	70.2(3)
Average:		1.479			

Deviations from the least squares plane (*cf. Fig. 1*)

Ce	0.00	O2	0.21
O1	−0.33	O2′	−0.21
O1′	0.33	O5	0.00

In the present structure also, cerium is coordinated by nine oxygen atoms; eight of these are sulfate oxygen atoms and one a water molecule. Four oxygen atoms belonging to different sulfate groups and the water molecule form a puckered five member ring around cerium perpendicular to the *c* axis. Two oxygen atoms belonging to the same sulfate group are coordinated above this ring, with a further two from a second sulfate group coordinated below. The latter, axial oxygen atoms, are at approximately right angles to each other. Thus, in the equatorial bonds the sulfate groups act as unidentate ligands and in the axial directions as bidentate ligands. The deviations from the least squares plane through the pentagon are found at the end of Table 2. The cerium atom was included in the calculation of the "best" plane. The coordination polyhedron with the atom-numbering system used in this report is shown in Fig. 1.

In the coordination sphere the nine Ce–O distances vary from 2.477 to 2.584 Å and the average value is 2.53 Å, in agreement with those found in $Ce_2(SO_4)_3.9H_2O$:[11] 2.51 Å, in $Na_3Ce(C_4H_4O_5)_3.9H_2O$:[13] 2.52 Å and in $Ce_2(C_2O_4)_3$

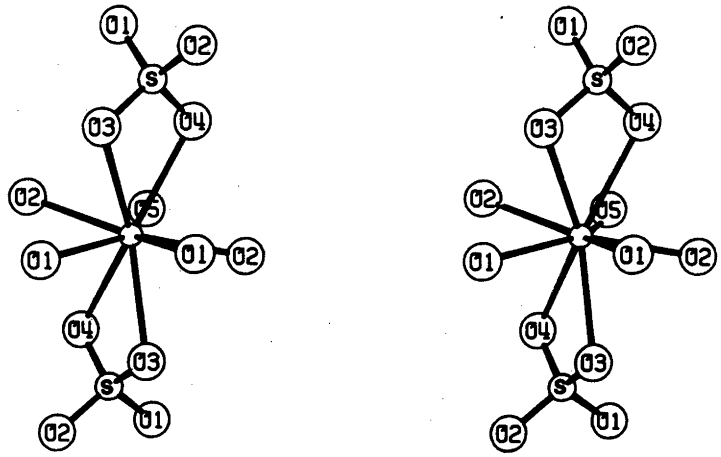

Fig. 1. A stereo view of the coordination polyhedron.

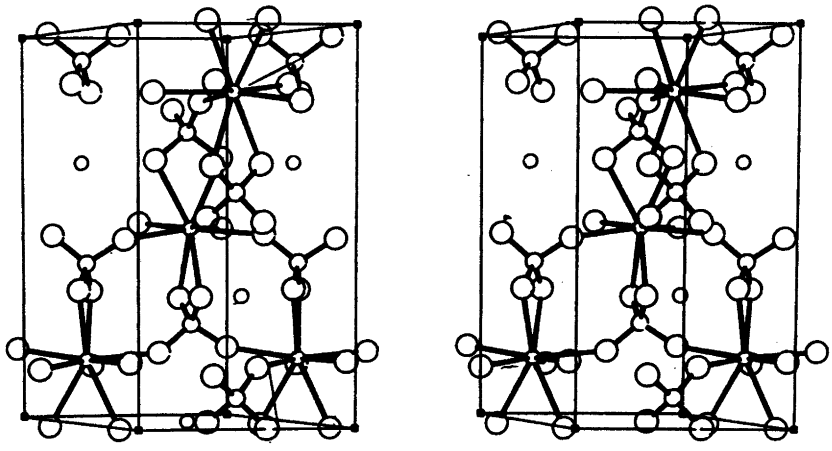

Fig. 2. A stereo drawing of the structure viewed approximately in the *b*-direction. The longest axis is the *c* axis.

$.10H_2O$:[14] 2.55 Å. Selected distances and angles are given in Table 2.

The structure is built up by Ce atoms joined by sulfate groups forming a three-dimensional network. This can be described in the following way. The sulfur atom has its x and y parameters almost equal which causes the six sulfur atoms in a unit cell to appear in pairs and defining three axes perpendicular to the xy plane. On approximately the same axes, between the sulfate groups, Na and Ce atoms alternate in filling the vacancies. A remaining void in the structure is occupied by a water molecule which completes the nine-coordination of cerium. A stereo view of the structure is shown in Fig. 2.

Na is surrounded by six oxygen atoms in the range 2.443 Å – 2.536 Å and another two at distances 2.870 Å. All eight oxygen atoms belong to sulfate groups. The coordination polyhedron does not permit a simple description.

The sulfate group is fairly regular, the angles being in the range 106.4 – 111.6°. However, the distance S – O2 is short, only 1.458 Å, while the other S – O distances are in the range 1.480 – 1.490 Å. Admittedly shorter S – O distances (in sulfate groups) have been reported but then only for terminal bonds. A conceivable explanation is that in this structure all four oxygen atoms are involved in bonds to cerium. These bonds are strong and add further geometrical constraints to the tetrahedron, deforming it somewhat. It should be remembered, however, that the difference in the bond lengths is just at the limit of significance (about three times the e. s. d.). In spite of the distortion, the average S – O bond length, 1.479 Å, is close to the usual average value.

The water molecule, O5, has four short distances to the sulfate oxygens, two to each of O1 and O2. The two O1 atoms are neighbours in the five-membered ring around cerium, whereas O5 belongs to an adjacent ring.

Hydrogen bonds are probably directed away from the cerium atom, eliminating the O5 – O2 interaction. Possible hydrogen bonds are thus two O5 – O1, 2.914 Å, the O1 – O5 – O1 angle being 63°.

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