Table 3. *Tetrahedral position angles, γ, and the ratios of octahedral–dodecahedral shared edge $(O\cdots O^v)$ to dodecahedral–dodecahedral shared edge $(O^v\cdots O^{ix})$ distances (Å) in $M_3^{2+}Al_2Si_3O_{12}$ garnets*

	γ^*	$(O\cdots O^v)/(O^v\cdots O^{ix})$	Ratio	Reference
Co(α)	28.07	2.639 (3)/2.705 (4)	0.976	Ohashi et al. (1981)
Co(β)	27.75	2.625 (1)/2.713 (1)	0.968	Present study
Mg	27.42	2.617 (3)/2.709 (3)	0.966	Novak & Gibbs (1971)
Fe	26.69	2.655 (2)/2.768 (3)	0.959	Novak & Gibbs (1971)
Mn	26.08	2.678 (2)/2.824 (3)	0.948	Novak & Gibbs (1971)
Ca, Mn	25.25	2.692 (2)†/2.879 (2)†	0.935	Novak & Gibbs (1971)
Ca	24.50	2.756 (2)/2.973 (2)	0.927	Novak & Gibbs (1971)
Cd	24.38	2.739 (8)/2.970 (10)	0.922	Ohashi et al. (1985)

* Born & Zemann (1964).
† Calculated by present authors.

The *SDP* program system (B. A. Frenz & Associates Inc., 1982) was employed.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: OH1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Redetermination of Sodium Cerium(III) Sulfate Monohydrate, NaCe(SO₄)₂.H₂O

ANTHONY C. BLACKBURN AND ROGER E. GERKIN*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA

Abstract

The structure of sodium cerium sulfate monohydrate, NaCe^{III}(SO$_4$)$_2$.H$_2$O, comprises distorted NaO$_6$ octahedra, CeO$_9$ polyhedra in the form of distorted tricapped trigonal prisms, and slightly irregular tetrahedral sulfate ions. This structure is isomorphic with that of NaLa^{III}(SO$_4$)$_2$.H$_2$O. All bonds fall within normal lim-

its. The sulfate ion manifested rigid-body behavior but neither of the cation complexes did. As in the previous structural analysis of the La analog [Blackburn & Gerkin (1994). *Acta Cryst.* C**50**, 835–838], the water molecule is modelled as having O-atom disorder but with an ordered H atom. Hydrogen bonds involve only sulfate O atoms as acceptors. The anisotropic atomic displacement parameters are found to be in good agreement with the corresponding parameters determined for the La analog, but in poor agreement with those previously reported for the title salt by Lindgren [*Acta Chem. Scand. Ser. A*, (1977), **31**, 591–594]. Taken together, the data establish that the lack of correction for absorption in the previous study of the Ce salt, rather than some intrinsic property of the Ce salt, is responsible for the displacement parameter discrepancies. The absolute structure has been determined.

Comment

This study of NaCe^{III}(SO$_4$)$_2$.H$_2$O was performed, following our study of the La^{III} analog (Blackburn & Gerkin, 1994), to allow direct comparisons with earlier results for the title salt (Lindgren, 1977). Of particular interest was the characterization of the anisotropic atomic displacement parameters since the corresponding values found in our study of the La analog differed notably from those reported for the Ce salt by Lindgren (1977). Moreover, the structural characterization of the water molecule was also of particular interest since in the La analog the water O atom was best modelled as disordered equally over two sites, but Lindgren's analysis did not ascribe such disorder to the Ce salt.

The experimental crystal belonged to the enantiomeric space group $P3_221$ (see *Experimental*), whereas our experimental crystal of the La analog and Lindgren's Ce crystal belonged to $P3_121$.

This salt is isomorphic with the La analog except for its handedness. The atom numbering corresponds with that chosen for the La analog, and structural descriptions given for the La analog (Blackburn & Gerkin, 1994) apply here with only minor changes.

In the distorted octahedral NaO$_6$ complex, the Na—O distances range from 2.447 (4) to 2.538 (3) Å [average 2.49 (4) Å] and the O—Na—O angles range from 71.7 (1) to 154.2 (2)° (Table 2). The next nearest atoms to Na, at distances of 2.849 (3) Å, are a symmetry-related pair of O(4) atoms. In the CeO$_9$ complex, the Ce—O distances range from 2.477 (3) to 2.582 (3) Å [average 2.53 (3) Å] while the O—Ce—O angles range from 54.4 (1) to 145.7 (1)° (Table 2). These values are in good agreement with our previous values for the La analog and also with those of Lindgren.

The sulfate ion is subject to no symmetry constraints and forms a slightly irregular tetrahedron. The observed S—O distances range from 1.465 (3) to 1.481 (3) Å [average 1.473 (6) Å] and the O—S—O angles range

from 105.7(2) to 112.0(2)° (Table 2). These values very closely match the corresponding values for the La analog. Lindgren's values for S—O distances ranged from 1.458(13) to 1.490(11) Å [average 1.479(13)Å] and the O—S—O angles ranged from 106.4(6) to 111.6(7)°. Thus, while the angular ranges and the average S—O bond distances are in good agreement, the range of S—O bond distances reported here for the Ce salt is only approximately one half of that reported earlier by Lindgren (the difference, however, is not statistically significant). As in the La analog, the hydrogen bonding in this salt involves only a single O donor atom, O(5), and only sulfate O atoms as acceptors. Again, only O(2) and O(4) are involved in substantial hydrogen bonds (Table 3).

Notable discrepancies between the present results and the earlier results of Lindgren are found in the anisotropic displacement parameters. Any numerical comparisons are rendered moot since Lindgren's U_{ij} values were found to yield several negative principal values for the displacement ellipsoids. Since our principal values for the title salt were uniformly positive, and are in good agreement with those of the La analog, the problem with Lindgren's analysis almost certainly arose from the lack of correction for absorption, rather than from some intrinsic property of his sample of the Ce salt.

The presence in the sample from gel crystal growth of single crystals of the title salt belonging to the enantiomeric space group $P3_121$ was confirmed.
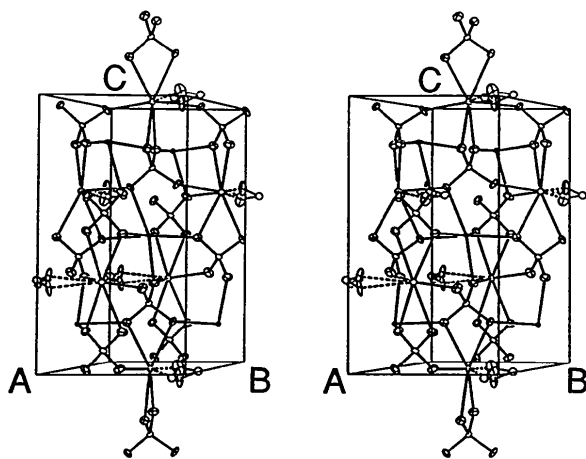

Fig. 1. An ORTEPII (Johnson, 1976) stereoview of a unit cell of sodium cerium(III) sulfate monohydrate at 296 K. Displacement ellipsoids have been drawn at 50% probability for all atoms except H, for which they have been set artificially small. The Na ions have been filled for contrast. Both positions of the disordered water O atom are shown. Hydrogen bonds have been omitted for clarity.

Experimental

Single crystals of NaCeᴵᴵᴵ(SO₄)₂.H₂O were prepared by gel-diffusion growth as described previously for the Laᴵᴵᴵ analog (Blackburn & Gerkin, 1994). The morphology of the crystals

was strikingly similar to that of the La analog: the crystals have six pentagonal side faces {010} with three capping pentagonal faces {101} (space group $P3_121$) or {101} (space group $P3_221$) at each end. The experimental sample was mounted with epoxy cement on a glass fiber.

Crystal data

NaCe(SO₄)₂.H₂O	Mo $K\alpha$ radiation
$M_r = 373.24$	$\lambda = 0.71073$ Å
Trigonal	Cell parameters from 25
$P3_221$	reflections
$a = 7.019(1)$ Å	$\theta = 16.3–17.4°$
$c = 12.925(2)$ Å	$\mu = 6.92$ mm⁻¹
$V = 551.4(2)$ Å³	$T = 296$ K
$Z = 3$	Capped hexagonal prism
$D_x = 3.372$ Mg m⁻³	$0.38 \times 0.13 \times 0.13$ mm
	Colorless

Data collection

AFC-5S diffractometer	$\theta_{max} = 27.5°$
ω scans	$h = 0 \rightarrow 7; -7 \rightarrow 0$
Absorption correction:	$k = 0 \rightarrow 7; -7 \rightarrow -1$
analytical	$l = -16 \rightarrow 16; -16 \rightarrow 16$
$T_{min} = 0.315, T_{max} =$	6 standard reflections
0.489	monitored every 150
1877 measured reflections	reflections
848 independent reflections	intensity variation: ±1.8%
831 observed reflections	(average maximum
$[I > 3\sigma(I)]$	relative intensity)
$R_{int} = 0.017$	

Refinement

Refinement on F	$\Delta\rho_{max} = 1.63$; next
$R = 0.017$	highest $= 0.56$ e Å⁻³
$wR = 0.030$	$\Delta\rho_{min} = -0.56$ e Å⁻³
$S = 1.72$	Extinction correction: none
831 reflections	Atomic scattering factors
60 parameters	from Stewart, Davidson &
H-atom parameters not	Simpson (1965) (H) and
refined (see below)	Cromer & Waber (1974)
$w = 1/\sigma^2(F)$	(O, Na, S, Ce)
$(\Delta/\sigma)_{max} < 0.01$	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ce	0.43376 (5)	0	2/3	0.00955 (10)
S	0.4528 (2)	0.0115 (2)	0.91277 (7)	0.0088 (2)
Na	0.4656 (3)	0	1/6	0.0070 (5)
O(1)	0.4972 (6)	−0.1215 (6)	0.9856 (2)	0.0177 (8)
O(2)	0.2599 (5)	−0.1308 (5)	0.8474 (2)	0.0157 (7)
O(3)	0.6372 (6)	0.1339 (6)	0.8404 (2)	0.0190 (8)
O(4)	0.4100 (6)	0.1627 (6)	0.9738 (2)	0.0188 (8)
O(5)†	0.0716 (11)	−0.0076 (18)	0.6450 (6)	0.0305 (16)

† Occupancy factor 0.5.

Table 2. *Selected geometric parameters* (Å, °)

Ce—S	3.183 (1)	S—O(1)	1.465 (3)
Ce—Sⁱ	3.183 (1)	S—O(2)	1.481 (3)
Ce—O(1ⁱⁱ)	2.477 (3)	S—O(3)	1.475 (4)

Ce—O(1^{iii})	2.477 (3)	S—O(4)	1.469 (3)
Ce—O(2)	2.582 (3)	Na—O(1^{vi})	2.538 (3)
Ce—O(2^i)	2.582 (3)	Na—O(1^i)	2.538 (3)
Ce—O(3)	2.573 (3)	Na—O(2^{vii})	2.493 (4)
Ce—O(3^i)	2.573 (3)	Na—O(2^{viii})	2.493 (4)
Ce—O(4^{iv})	2.496 (3)	Na—O(3^{ix})	2.447 (4)
Ce—O(4^v)	2.496 (3)	Na—O(3^x)	2.447 (4)
Ce—O(5)	2.530 (6)	O(5)—H	0.97
Ce—O(5^i)	2.530 (6)	O(5)—H^i	0.97
O(1^{ii})—Ce—O(1^{iii})	139.7 (2)	O(1)—S—O(2)	110.6 (2)
O(1^{ii})—Ce—O(2)	71.22 (10)	O(1)—S—O(3)	112.0 (2)
O(1^{ii})—Ce—O(3)	119.3 (1)	O(1)—S—O(4)	107.5 (2)
O(1^{ii})—Ce—O(4^{iv})	145.5 (1)	O(2)—S—O(3)	105.7 (2)
O(1^{ii})—Ce—O(5)	68.4 (3)	O(2)—S—O(4)	110.2 (2)
O(1^{ii})—Ce—O(5^i)	71.5 (3)	O(3)—S—O(4)	110.9 (2)
O(2)—Ce—O(2^i)	145.7 (1)	O(1^{vi})—Na—O(1^i)	150.4 (2)
O(2)—Ce—O(4^{iv})	122.68 (9)	O(1^{vi})—Na—O(2^{vii})	71.7 (1)
O(2)—Ce—O(5)	78.5 (2)	O(1^i)—Na—O(2^{vii})	85.4 (1)
O(2)—Ce—O(3)	54.4 (1)	O(1^{iv})—Na—O(3^{ix})	79.3 (1)
O(3)—Ce—O(3^i)	136.3 (2)	O(1^i)—Na—O(3^x)	114.00 (10)
O(3)—Ce—O(4^{iv})	68.6 (1)	O(2^{viii})—Na—O(2^{vii})	79.2 (2)
O(3)—Ce—O(5)	118.2 (2)	O(2^{viii})—Na—O(3^x)	76.3 (1)
O(4^{iv})—Ce—O(4^v)	76.2 (2)	O(2^{vii})—Na—O(3^x)	154.2 (2)
O(4^{iv})—Ce—O(5)	141.1 (3)	O(3^x)—Na—O(3^{ix})	128.9 (2)

Symmetry codes: (i) $x - y, -y, \frac{4}{3} - z$; (ii) $-y, x - y - 1, z - \frac{1}{3}$; (iii) $1 - x, 1 + y - x, \frac{5}{3} - z$; (iv) $1 - y, x - y, z - \frac{1}{3}$; (v) $1 - x, y - x, \frac{5}{3} - z$; (vi) $x, y, z - 1$; (vii) $1 + y - x, -x, z - \frac{2}{3}$; (viii) $1 + y, x, 1 - z$; (ix) $y, x - 1, 1 - z$; (x) $1 + y - x, 1 - x, z - \frac{2}{3}$.

Table 3. Hydrogen-bonding geometry (Å, °)

No e.s.d.'s are given for H⋯O(acceptor) distances (H⋯A) since H-atom positions are fixed. The criteria for inclusion in this tabulation are (a) the H atom involved in the hydrogen bond must be closer to the O(acceptor) atom than is the O(donor) atom (D), and (b) the O(donor) to O(acceptor) distance (D⋯A) is < 3.2 Å.

D—H⋯A	H⋯A	D⋯A	D—H⋯A
O(5)—H⋯O(1^{iii})	2.70	2.926 (10)	93.7 (4)
O(5)—H⋯O(4^{xi})	2.16	2.976 (9)	140.3 (4)
O(5)—H⋯O(2^{xi})	2.50	3.114 (11)	120.9 (5)
O(5)—H^i⋯O(1^{ii})	2.70	2.815 (11)	86.8 (5)
O(5)—H^i⋯O(4^{xii})	2.16	2.992 (8)	142.8 (5)

Symmetry codes: (i) $x - y, -y, \frac{4}{3} - z$; (ii) $-y, x - y - 1, z - \frac{1}{3}$; (iii) $1 - x, 1 + y - x, \frac{5}{3} - z$; (xi) $-y, x - y, z - \frac{1}{3}$; (xii) $-x, y - x, \frac{5}{3} - z$.

Unit-cell parameters were obtained from a symmetry-constrained least-squares fit. Scan widths were $(1.50 + 0.35\tan\theta)°$ in ω and the ratio of background to scan time was 0.5. No decay correction was made but the data were corrected for Lorentz and polarization effects. An analytical absorption correction was applied using AGNOST (de Meulenaer & Tompa, 1965). The intensity data were consistent with Laue group $\bar{3}m1$; the observed reflection-limiting condition $(00l, l = 3n)$ was then consistent with only the enantiomeric space groups $P3_121$ and $P3_221$. It was shown for the La analog (Blackburn & Gerkin, 1994) that capping faces $\{101\}$ are associated with $P3_121$ samples while capping faces $\{\bar{1}01\}$ are associated with $P3_221$ samples. For the experimental sample the space group $P3_221$ was given initial preference on this basis. The atomic coordinates of Na, S and La from the La analog were used as starting positions for Na, S and Ce in the present study except that each z coordinate was replaced by $-z$. Fourier difference methods were used to assign the remaining atoms. When the structure was analyzed in the potential alternative space group $P3_121$, the final R factor increased by 0.97%. Moreover, in a separate calculation, SHELXL93 (Sheldrick, 1993) was used to refine the Flack x

parameter (Flack, 1983; Bernardinelli & Flack, 1985) simultaneously with the coordinates in $P3_221$ and gave the value $x = 0.061$ (29). These results confirmed the space group and coordinate assignments given in this report, and thus determined the absolute structure.

The refinement of the water O atom, O(5), proceeded just as described for its O(5) analog in the La salt (Blackburn & Gerkin, 1994) and was therefore modelled as disordered equally over two sites 0.57 Å apart. The H atom was modelled as ordered, also as previously: since the H-atom position was not determinable from difference maps it was fixed consistent with average water molecule geometry for the same hydrate class (N) as was observed for the La analog (Blackburn & Gerkin, 1994). Accordingly, the water O—H distance is 0.97 Å, the H—O—H angle is 104.7° and the Ce—O(5)—H angles are 120.1 (1)°. The H-atom isotropic displacement parameter was taken from the neutron-diffraction powder data for the La analog (W. J. Reppart, private communication).

The maximum positive residual electron density, 1.63 e Å^{-3}, occurred 0.07 Å from the Na atom while the next highest, 0.56 e Å^{-3}, occurred 2.52 and 2.61 Å from Na and Ce, respectively. The maximum negative density, -0.56 e Å^{-3}, occurred 0.44 Å from O(5).

Rigid-body analysis of the NaO polyhedron, the CeO polyhedron and the sulfate ion was performed using the program THMA11 (Trueblood, 1986), which is based on the work of Schomaker & Trueblood (1968). Neither the NaO nor the CeO polyhedron conformed to rigid-body behavior, but the sulfate ion did. The average magnitude of the differences in the mean-square displacement amplitudes along the interatomic vectors for the ten unique atom pairs of the sulfate ion was 28 (22) × 10^{-4} Å^2. The Hirshfeld (1976) rigid-bond test, extended as described by Rosenfield, Trueblood & Dunitz (1978), is satisfied and the corrected S—O bond lengths are given in this report. The rigid-body-corrected S—O bond distances are as follows: S—O(1) 1.475, S—O(2) 1.488, S—O(3) 1.485, S—O(4) 1.479 Å. These values may be compared with the corresponding rigid-body values found for the La analog: 1.481, 1.484, 1.486 and 1.475 Å, respectively.

Data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1988). Cell refinement: MSC/AFC Diffractometer Control Software. Data reduction: TEXSAN (Molecular Structure Corporation, 1989). Program(s) used to refine structure: TEXSAN. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: TEXSAN.

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Ta$_3$S$_{2-x}$Se$_x$, Partial Substitution of Selenium for Sulfur into a Tantalum-Rich Sulfide

Thomas Degen and Bernd Harbrecht

Institut für Anorganische Chemie, Universität Bonn, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany

Abstract

In the pentagonal antiprismatic columnar structure of Ta$_3$S$_2$, sulfur can be partially replaced by selenium. Selenium accumulates preferentially at one of two independent sites, which leads to unusually short Ch—Ch [2.973 (3) Å] contacts, where Ch denotes a chalcogen site.

Comment

The structural chemistries of tantalum-rich sulfides and selenides differ drastically. Whereas the structure of Ta$_2$S (Franzen & Smeggil, 1969) results from the interpenetration of centred Ta$_{13}$ icosahedra along a

pseudo fivefold axis of symmetry, Ta$_2$Se forms a unique layered-type structure which is symmetry related to b.c.c. Ta (Harbrecht, 1989). In order to gain information about the relative stability of the distinct structural arrangements, we systematically investigated the Ta-rich region of the ternary Ta–S–Se system.

Entropically stabilized high-temperature phases of Ta$_5$(S,Se)$_2$, the (Nb,Ta)$_5$S$_2$ structure type (Yao & Franzen, 1991) and Ta$_9$(S,Se)$_4$ are accessible above temperatures of approximately 1700 K. These b.c.c.-related phases have no pendants in the binary systems (Harbrecht & Degen, 1993). In contrast to earlier reports (Nanjundaswamy & Hughbanks, 1992), we found that a significant amount of selenium can be substituted for sulfur in the structures of the sulfides. Such a mixed chalcogenide of the Ta$_3$S$_2$ structure type (Wada & Onoda, 1989; Kim, Nanjundaswamy & Hughbanks, 1991) is the subject of this report.

The structure of Ta$_3$(S,Se)$_2$ consists of distorted Ta$_{13}$ icosahedra which interpenetrate along the c axis forming columns of face-shared pentagonal antiprismatic clusters, $^1_\infty$[TaTa$_{10/2}$]. Very short Ta—Ta contacts exist [Ta4—Ta4 2.811 (2) Å, compared to 2.860 Å in b.c.c.-Ta] in the centre of the pentagonal antiprismatic TaTa$_{10}$ clusters. The columns of condensed clusters are linked to one another, parallel to a, by weaker Ta1—Ta3 [3.158 (1) Å] and Ta3—Ta3 [3.650 (1) Å] contacts and strong heteronuclear bonds Ch2—Ta [2.455 (2)–2.492 (2) Å], where Ch is S or Se.

As can be seen from Fig. 2, these complex layers are also covered by Ch1 over triangular faces [Ch1—Ta1 and 2 × Ch1—Ta2 2.472 (2)–2.529 (2) Å]. Heteronuclear interlayer contacts seem to be weaker [Ch1—Ta2 2.709 (2), Ch2—Ta1 2.547 (2) Å] than interactions within the two-dimensional arrays. The specific stacking of the layers along b results in empty channels running
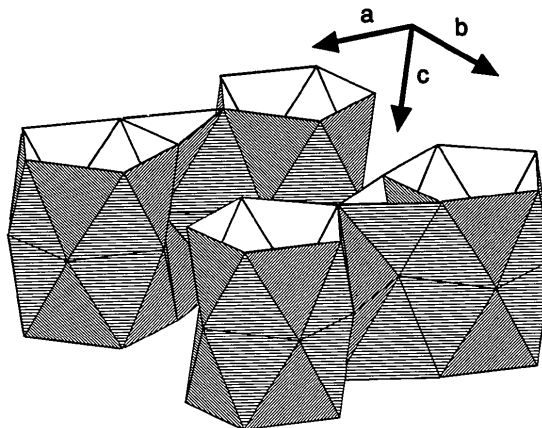

Fig. 1. Polyhedral representation of the tantalum partial structure of Ta$_3$(S,Se)$_2$ depicted as pentagonal antiprismatic columns connected *via* Ta$_4$ tetrahedra. Since the columns are centred by Ta4 (which are omitted for clarity) the layers are tetrahedrally close packed.