

INORGANIC COMPOUNDS

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Sodium Lanthanum(III) Sulfate Monohydrate, $\text{NaLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$

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Abstract

The structure of $\text{NaLa}^{\text{III}}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ consists of distorted $\text{Na}-\text{O}_6$ octahedra, $\text{La}-\text{O}_9$ complexes in the form of distorted tricapped trigonal prisms, and slightly irregular tetrahedral sulfate ions. All bond distances fall within normal limits. The sulfate ions manifest rigid-body behavior but this is not the case for either of the cation complexes. The single water molecule is modelled as having O-atom disorder but an ordered H atom. Hydrogen bonds involve only sulfate O atoms as acceptors. The absolute structure has been determined.

Comment

Our interest in the structure of single-crystalline $\text{NaLa}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ concerned its hydrogen-bonding behavior. Further interest lay in potential comparisons with the structure of single-crystalline $\text{NaCe}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ as reported by Lindgren (1977).

The experimental crystal was shown to belong to the space group $P3_121$ (see *Experimental*). The same space group was chosen by Lindgren (1977), but without explicit justification *vis-à-vis* the enantiomorph $P3_221$, for analysis of single-crystal data from the Ce analog. Nevertheless, the particular crystals of the two salts studied by Lindgren and reported here are isostructural.

In this structure there are two cation complexes and a sulfate anion. The distorted octahedral $\text{Na}-\text{O}_6$ complex (Fig. 1*a*) involves symmetry-related pairs of O(1), O(2) and O(3) atoms from sulfate anions, with $\text{Na}-\text{O}$ distances ranging from 2.467 (3) to 2.530 (2) Å [average 2.50 (3) Å] and with $\text{O}-\text{Na}-\text{O}$ angles ranging from 72.2 (1) to 154.6 (1)° (Table 2). The next-nearest atoms, separated by 2.857 (3) Å, are a symmetry-related pair of O(4) atoms also from sulfate anions. These values are in good agreement with those reported for the Ce analog by Lindgren (1977).

The $\text{La}-\text{O}_9$ complex, which may be described as a distorted tricapped trigonal prism (Fig. 1*b*), involves symmetry-related pairs of O(1), O(2), O(3) and O(4) atoms from sulfate anions with an additional O atom, O(5), from the water molecule. The $\text{La}-\text{O}$ distances range from 2.490 (3) to 2.600 (2) Å [average 2.55 (5) Å] while the $\text{O}-\text{La}-\text{O}$ angles range from 54.0 (1) to 146.3 (1)° (Table 2). These values also agree well with those for the Ce analog (Lindgren, 1977).

The sulfate anion is subject to no symmetry constraints and forms a slightly irregular tetrahedron. The observed $\text{S}-\text{O}$ distances range from 1.466 (2) to 1.478 (3) Å [average 1.474 (5) Å] and the $\text{O}-\text{S}-\text{O}$

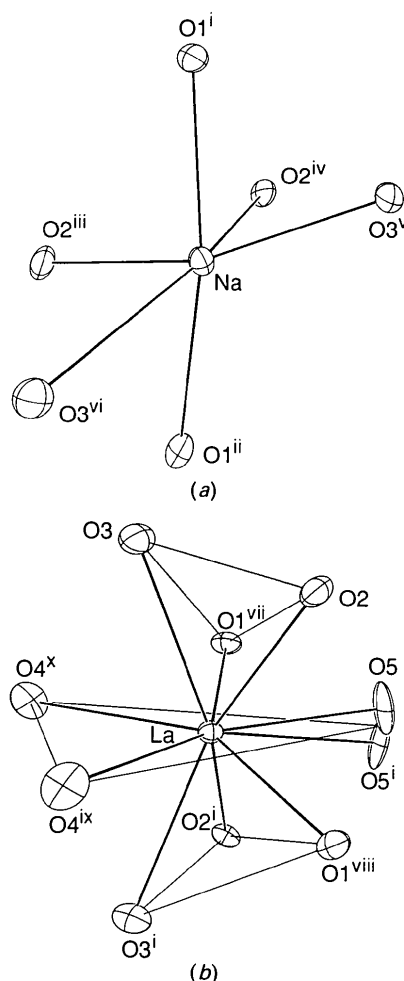


Fig. 1. ORTEPII (Johnson, 1976) views of (a) the distorted octahedral $\text{Na}-\text{O}_6$ complex and (b) the distorted tricapped trigonal prismatic $\text{La}-\text{O}_9$ complex in sodium lanthanum(III) sulfate monohydrate at 296 K. Displacement ellipsoids have been drawn at 50% probability for all atoms.

angles range from 105.8 (1) to 112.0 (1)° (Table 2). For the Ce analog, the S—O distances were in the range 1.458 (13)–1.490 (11) Å [average, 1.479 (13) Å] and the O—S—O angles varied between 106.4 (6) and 111.6 (7)°. Thus, while the average S—O bond distances are in good agreement, the range of S—O bond distances reported here for the La salt is only approximately a third of that reported for the Ce salt by Lindgren (1977).

The hydrogen-bonding pattern in this salt is rather simple: there is only a single O donor atom, O(5), and hydrogen bonds involve only sulfate O atoms as acceptors; only O(4) and O(2) are involved in substantial hydrogen bonds (see Table 3 and Fig. 2). Although Lindgren (1977) did not resolve the H atom in the Ce analog, his inferences concerning the hydrogen bonding are largely consistent with the

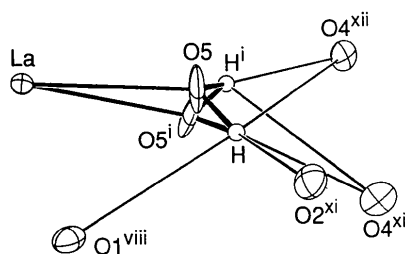


Fig. 2. An ORTEPII (Johnson, 1976) view of a portion of the near neighborhood of the water molecule in the title salt. Only those O(acceptor) atoms which form acceptable hydrogen bonds with O(5) as the donor O atom are included, though the alternative position of the disordered O atom, O(5ⁱ), is also shown. Displacement ellipsoids have been drawn at 50% probability for all atoms except H, for which they have been set artificially small. For numerical details, see Table 3.

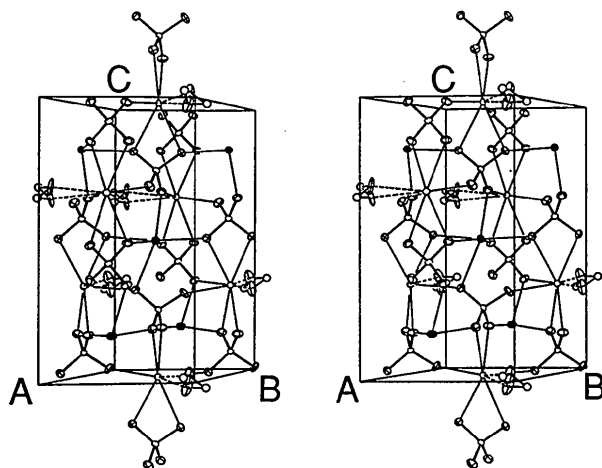


Fig. 3. An ORTEPII (Johnson, 1976) stereoview of a unit cell of sodium lanthanum(III) sulfate monohydrate at 296 K. Displacement ellipsoids have been drawn at 50% probability for all atoms except H, for which they have been set artificially small. The Na ions have been filled for contrast. Both positions of the disordered water O atom are shown. Hydrogen bonds have been omitted for clarity.

present conclusions, especially considering that the water O atom in the Ce analog was assigned to a special position whereas in the present analysis it was not. A unit cell of the title structure is shown in Fig 3.

Notable discrepancies between the present work on La and that on the Ce analog are found in some values of the anisotropic displacement parameters. For example, Lindgren (1977) gives a value of ~ 6.0 for the ratio of U_{22} for the S atom to that for Na, while the value found in the present study is ~ 1.0 . It appears that Lindgren's values may be unreliable because although $\mu \approx 6 \text{ mm}^{-1}$, there was no correction for absorption.

The presence in the gel crystal-growth of single crystals of the title salt belonging to the enantiomeric space group $P3_221$ was confirmed.

The structure of anhydrous sodium lanthanum sulfate has been reported by Chizhov, Pokrovskii & Kovba (1981), but it shows little relation to the structure of the hydrated salt reported here.

Experimental

Since direct mixing of aqueous solutions of sodium and lanthanum sulfates in near-stoichiometric proportion produced only very small crystals of NaLa(SO₄)₂·H₂O, gel-diffusion growth was employed. A V-shaped tube was filled partially with silica gel which was then rinsed with dilute HNO₃ until the effluent was slightly acidic. Aqueous sodium sulfate was placed in one arm of the tube and aqueous lanthanum nitrate in the other. Usable crystals of NaLa(SO₄)₂·H₂O grew by diffusion in approximately three weeks in the form of hexagonal columns terminated at each end by three pentagonal faces {101} or {101} and with each of the six side faces {010} also pentagonal.

Crystal data

NaLa(SO₄)₂·H₂O
 $M_r = 372.03$
 Trigonal
 $P3_221$
 $a = 7.0557 (7) \text{ \AA}$
 $c = 12.9669 (9) \text{ \AA}$
 $V = 559.04 (12) \text{ \AA}^3$
 $Z = 3$
 $D_x = 3.315 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 14.2\text{--}14.9^\circ$
 $\mu = 6.37 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Clear terminated-hexagonal column
 $0.39 \times 0.13 \times 0.13 \text{ mm}$
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction:
 analytical (AGNOST;
 de Meulenaer & Tompa,
 1965)
 $T_{\min} = 0.419$, $T_{\max} =$
 0.536 , $T_{\text{mean}} = 0.487$

$\theta_{\max} = 27.5^\circ$
 Part I
 $h = 0 \rightarrow 7$
 $k = 0 \rightarrow 7$
 $l = -16 \rightarrow 16$
 Part II
 $h = -7 \rightarrow 0$
 $k = -7 \rightarrow 0$
 $l = -16 \rightarrow 16$

2118 measured reflections
874 independent reflections
851 observed reflections
 $[I > 3\sigma(I)]$
 $R_{\text{int}} = 0.013$

Refinement

Refinement on F^2 $R = 0.014$ $wR = 0.024$ $S = 1.39$

851 reflections

61 parameters

 $w = \sigma_F^{-2}$, where $\sigma_F^{-2} = \sigma_I^2/2FLp$, $\sigma_I^2 = \sigma_{\text{cs}}^2(I) + (0.03I)^2$ $(\Delta/\sigma)_{\text{max}} = 0.01$

6 standard reflections
monitored every 150
reflections
intensity variation: $\pm 0.7\%$

 $\Delta\rho_{\text{max}} = 1.02 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.42 \text{ e } \text{\AA}^{-3}$

Extinction correction:

Zachariasen (1963, 1968)

Extinction coefficient:

 $1.33 (26) \times 10^{-6}$

Atomic scattering factors

from Cromer & Waber
(1974) (non-H) and Stewart,
Davidson & Simpson,
1965) (H)

O(1^{vii})—La—O(5) 68.4 (2)
O(1^{viii})—La—O(5) 71.5 (2)
O(2)—La—O(5) 78.5 (2)
O(3)—La—O(5) 117.8 (2)
O(4^{ix})—La—O(5) 141.4 (2)

Sulfate anion:

rigid body (r.b.) I

r.b. corrected

S—O(1)	1.473 (3)	1.481	O(1)—S—O(2)	110.6 (1)
S—O(2)	1.478 (2)	1.484	O(1)—S—O(3)	112.0 (2)
S—O(3)	1.478 (3)	1.486	O(1)—S—O(4)	107.5 (1)
S—O(4)	1.466 (2)	1.475	O(2)—S—O(3)	105.8 (1)
			O(2)—S—O(4)	110.1 (2)
			O(3)—S—O(4)	110.9 (2)

Water molecule†

O(5)—H	0.89	H—O(5)—H [†]	94.5
O(5)—H [†]	0.97		

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

* Half occupancy.

† E.s.d.'s not provided since H fixed.

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2) for sodium lanthanum(III) sulfate monohydrate at 296 K with e.s.d.'s in parentheses

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B_{eq}/B
La	0.43318 (4)	0	1/3	0.76 (1)
S	0.4528 (1)	0.0118 (1)	0.08645 (5)	0.75 (2)
Na	0.4681 (3)	0	5/6	1.12 (8)
O(1)	0.4979 (4)	-0.1207 (4)	0.0134 (2)	1.37 (8)
O(2)	0.2614 (4)	-0.1299 (4)	0.1515 (2)	1.28 (8)
O(3)	0.6367 (5)	0.1347 (4)	0.1586 (2)	1.42 (8)
O(4)	0.4093 (5)	0.1613 (4)	0.0257 (2)	1.49 (8)
O(5)†	0.0710 (10)	-0.0080 (15)	0.3539 (5)	2.5
H†	0.0456	0.1032	0.3539	3.7

† For details of refinement, see text below.

‡ Isotropic, fixed at $1.5 \times B_{\text{eq}}$ of O(5) (see text below).

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$) in sodium lanthanum(III) sulfate monohydrate at 296 K with e.s.d.'s in parentheses

Na—O ₆ polyhedron			
Na—O(1 ⁱ)	2.530 (2)	O(1 ⁱ)—Na—O(1 ⁱⁱ)	150.9 (2)
Na—O(1 ⁱⁱ)	2.530 (2)	O(1 ⁱ)—Na—O(2 ⁱⁱⁱ)	85.5 (1)
Na—O(2 ⁱⁱⁱ)	2.501 (3)	O(1 ⁱ)—Na—O(2 ^{iv})	72.2 (1)
Na—O(2 ^{iv})	2.501 (3)	O(1 ⁱ)—Na—O(3 ^v)	78.9 (1)
Na—O(3 ^v)	2.467 (3)	O(1 ⁱ)—Na—O(3 ^{vi})	114.2 (1)
Na—O(3 ^{vi})	2.467 (3)	O(2 ⁱⁱⁱ)—Na—O(2 ^{iv})	80.1 (1)
		O(2 ⁱⁱⁱ)—Na—O(3 ^v)	154.6 (1)
		O(2 ⁱⁱⁱ)—Na—O(3 ^{vi})	76.2 (1)
		O(3 ^v)—Na—O(3 ^{vi})	128.6 (2)
Not included in polyhedron			
Na—O(4 ^{ix})	2.857 (3)		
Na—O(4 ^{ix})	2.857 (3)		
La—O ₉ polyhedron			
La—O(1 ^{vii})	2.490 (3)	O(1 ^{vii})—La—O(1 ^{viii})	139.6 (1)
La—O(1 ^{viii})	2.490 (3)	O(2)—La—O(2 ⁱ)	146.3 (1)
La—O(2)	2.600 (2)	O(3)—La—O(3 ⁱ)	136.6 (1)
La—O(2 ⁱ)	2.600 (2)	O(4 ^{ix})—La—O(4 ^{ix})	76.0 (1)
La—O(3)	2.596 (2)	O(1 ^{vii})—La—O(2)	71.2 (1)
La—O(3 ⁱ)	2.596 (2)	O(1 ^{vii})—La—O(3)	119.1 (1)
La—O(4 ^{ix})	2.521 (3)	O(1 ^{vii})—La—O(4 ^{ix})	145.6 (1)
La—O(4 ^{ix})	2.521 (3)	O(2)—La—O(3)	54.0 (1)
La—O(5)*	2.541 (5)	O(2)—La—O(4 ^{ix})	122.1 (1)
La—O(5 ⁱ)*	2.541 (5)	O(3)—La—O(4 ^{ix})	68.5 (1)

Table 3. Hydrogen-bond geometry (\AA , $^\circ$) in sodium lanthanum(III) sulfate monohydrate with e.s.d.'s in parentheses

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 $\leq 3.2 \text{ \AA}$.

D—H...A	D...A	H...A	D—H...A
O(5)—H...O(1 ^{viii})	2.939 (8)	2.85	87.1 (4)
O(5)—H...O(4 ^{ix})	2.986 (7)	2.16	154.2 (4)
O(5)—H [†] ...O(4 ^{ix})	2.996 (6)	2.16	142.8 (4)
O(5)—H...O(4 ^{ix})	2.996 (6)	2.97	82.8 (4)
O(5)—H [†] ...O(4 ^{ix})	2.986 (7)	2.97	81.2 (4)
O(5)—H...O(2 ^{xi})	3.134 (8)	2.48	130.7 (4)

Symmetry codes: (i) $x - y, -y, \frac{2}{3} - z$; (viii) $1 - x, 1 + y - x, \frac{1}{3} - z$;
(xi) $-y, x - y, \frac{1}{3} + z$; (xii) $-x, -x + y, \frac{1}{3} - z$.

The experimental sample was mounted with epoxy cement on a glass fiber and analyzed with graphite-monochromated radiation. The unit-cell parameters were obtained from a symmetry-constrained least-squares fit. The scan widths were $(1.50 + 0.35 \tan \theta)^\circ$ 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-polarization and absorption effects.

The intensities were consistent with Laue group $\bar{3}m1$. The systematic absences ($00l, l \neq 3n$) were consistent with only the two enantiomeric space groups $P3_121$ and $P3_221$. Initially, $P3_121$ (No. 152) was chosen arbitrarily. Initial coordinates for La were obtained from a Patterson map and Fourier difference methods were used to assign the remaining atoms. Full-matrix least-squares refinement was performed using the TEXSAN (Molecular Structure Corporation, 1989) structure analysis package. An extinction coefficient was included in the least-squares refinement; the maximum effect of extinction was 4.5% of F_o for O20.

Since the structure was analyzed in an enantiomeric space group, R and wR were obtained for least-squares anisotropic convergence of all the non-H atoms for absorption-corrected

data with both normal and non-normal senses of the anomalous-dispersion effect (Stout & Jensen, 1989). For the non-normal sense $R = 0.0249$ and $wR = 0.0453$, whereas for the normal sense $R = 0.0147$ and $wR = 0.0249$. In separate calculations, *SHELXL* (Sheldrick, 1994) was used to refine the Flack x parameter (Flack, 1983; Bernardinelli & Flack, 1985) simultaneously with the coordinates and yielded the value $x = 0.037$ (20). These results demonstrate decisively that the space-group assignment and the coordinates (as given in Table 1) have been chosen correctly, determining the absolute structure.

The positional and displacement parameters for the water molecule are uncertain. One analysis places the water O atom, O(5), at a special position ($x, 0, \frac{1}{3}$) whereupon its B_{eq} refines to a value almost four times the corresponding mean value for the sulfate O atoms O(1)–O(4); its U_{33} is almost ten times the corresponding mean value for the sulfate O atoms. An alternative analysis, adopted for this report, involves disordering O(5) by moving it with half-occupancy 0.28 Å from the special position given above (see Fig. 2). The final B_{eq} value for O(5) in this second model is approximately 1.8 times the corresponding mean value for the sulfate O atoms. For the final refinement cycles, a water H atom, H, was assigned to a fixed position obtained from a difference Fourier map with an isotropic displacement parameter fixed at 1.5 times B_{eq} of O(5). It should be noted that all these variations in O(5) and H assignments produced very small effects on any of the other atoms; for example, the average maximum change in the positional parameters of the sulfate O atoms was only 1.3 times the corresponding e.s.d.'s.

The maximum positive residual electron density ($1.02 \text{ e } \text{Å}^{-3}$) occurred 0.29 Å from Na while the next highest ($0.42 \text{ e } \text{Å}^{-3}$) occurred 0.43 Å from O(2); the maximum negative peak ($-0.42 \text{ e } \text{Å}^{-3}$) occurred 0.65 Å from S.

Rigid-body analysis of the Na–O polyhedron, the La–O 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 Na–O nor the La–O 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 $15(16) \times 10^{-4} \text{ Å}^2$. 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 Table 2.

Owing to the lack of a single definitive interpretation of the water molecule geometry (as described above), the water H-atom position is reported as found but has not been adjusted to account for the usual foreshortening of O–H distances observed in X-ray determinations.

We thank Dr W. J. Reppart for interesting us in this system and Dr J. C. Gallucci for help of various sorts. We gratefully acknowledge the partial support of this research through the purchase of the diffractometer system by an NIH grant.

Lists of structure factors, anisotropic displacement parameters and material relating to the rigid-body analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71737 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1065]

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NaScSi₂O₆

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Abstract

The structure of NaScSi₂O₆ pyroxene formed at 6 GPa pressure, is isomorphous with that of NaScSi₂O₆ formed at atmospheric pressure. However, the cell parameters and the atomic coordinates are different. The NaScSi₂O₆ pyroxene obtained by the quenching method is sluggish in changing structure and the structure obtained is not always that of the equilibrium state at room temperature and atmospheric pressure.

Comment

The structure of NaScSi₂O₆ pyroxene synthesized at atmospheric pressure (Ito & Frondel, 1968) was