REGULAR STRUCTURAL PAPERS

Structure of an Acid Neodymium(III) Cerium(IV) Sulfate Hydrate, $H_9Nd_7Ce_6(SO_4)_{27}.72.33H_2O$

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Abstract

In cerium(IV) neodymium(III) hydrogen sulfate hydrate, layers perpendicular to c contain tricapped trigonal prismatic Ce^{IV} in $Ce_2(SO_4)_9^{10-}$ anions, with bidentate and bridging sulfate groups. These anions form sulfate bridges to tricapped trigonal prismatic Nd^{III} with six water and three sulfate ligands. Nd^{III} ions occur in general positions and in 6 special positions. The structure contains lattice water in both infinite and blocked channels parallel to c.

Comment

The existence of acid sulfato complexes containing Ce^{IV} and Ln^{III} (where Ln = La, Ce, Pr, Nd) was first reported in 1843 (Hermann). Mellor (1924) reviewed the confusion which had developed regarding these compounds. Reported analyses varied widely, particularly in the free acid and water content. The favoured formula was $LnHCe(SO_4)_3.12H_2O$, for pleochroic hexagonal crystals with c/a 2.6669, determined from optical measurements on the neodymium compound (Brauner, 1904). No work appears to have been performed on these compounds for many years.

Samples of Ce^{III}/Ce^{IV}, Nd^{III}/Ce^{IV} and Tb^{III}/Ce^{IV} compounds have now been prepared. These all have very similar unit cells with hexagonal symmetry. The structure of the Nd^{III} compound has been determined. The c/a ratio is 1.306, *i.e.* very close to half that suggested from the early optical measurements. The composition found from the crystal structure determination (14Nd, 12Ce, 54SO$_4$, >142H$_2$O, 18H$^+$) is close to Brauner's formulation (12Nd, 12Ce, 48SO$_4$, 144H$_2$O, 12H$^+$).

Cerium and neodymium have very similar scattering factors. In the early stages of the structure solution all lanthanides were assigned as neodymium. The final choice was based on the Ln—O distances and the larger apparent thermal parameters for the Ce atoms when assigned as Nd. The ranges of Ln—O distances in the present compound

are 2.477–2.520 Å for Nd1, 2.483–2.556 Å for Nd2 and 2.273–2.487 Å for Ce3, with mean values 2.496, 2.507 and 2.380 Å, respectively. In $Ln_2(SO_4)_3.8H_2O$, the range of Ln—O distances is 2.36–2.57 Å for Pr^{3+} (Sherry, 1976) and 2.30–2.49 Å for Sm^{3+} (Podberezskaja & Borosin, 1976). In $Nd_2(SO_4)_3.5H_2O$, the mean Nd—O distance is 2.48 Å (Larsson, Linderbrandt, Niinisto & Skoglund, 1973). The average Ce—O distance in $Ce(SO_4)_2.4H_2O$ is 2.326 Å (Lindgren, 1977).

The two identical layers which make up the cell are related by an n-glide perpendicular to c. Nd2 occupies the $2d$ position (6) on the mirror plane within the layer. Nd1 and Ce3 are in general positions close to ($\frac{1}{3}$, $\frac{1}{3}$, z) and (0, $\frac{1}{3}$, z) (Fig. 1). For example, the position near (0, $\frac{1}{3}$, z) is occupied by two Ce3 [z = 0.250 ($\pm$105)] and two Nd1 [z = 0.750 ($\pm$143)] (Fig. 2). The coordination of the metal ions is summarized in Figs. 2 and 3. Each of the metal ions has tricapped trigonal prismatic coordination. Nd2 has exact trigonal symmetry, with three water molecules (O1) above and below the median plane of three sulfate O atoms (O21). The sulfate group based on S20 also uses O23 and O23$'$ to bridge Ce3 and Ce3$'$. (Ce3$'$ *etc.* are related to the parent atoms by the mirror plane perpendicular to c at z = 0.25.) This bridging is completed by O13, O13$'$ and O33, O33$'$. The average bridging Ce—O distance is 2.279 Å. Bidentate sulfate groups S40, S50 and S60 complete the environment of Ce3. O43, O53, O63 form the outer plane, with an average Ce—O distance of 2.387 Å. O44, O54, O64 form the median plane, with an average Ce—O distance of 2.474 Å.

Atoms symmetry related to O42, O52 and O62 form the median plane for Nd1, the coordination of which is completed by water molecules O2, O4 and O5 on the outside of the layer and O6, O7 and O3 towards the mirror plane at the centre of the layer. The pairs of Nd1 ions
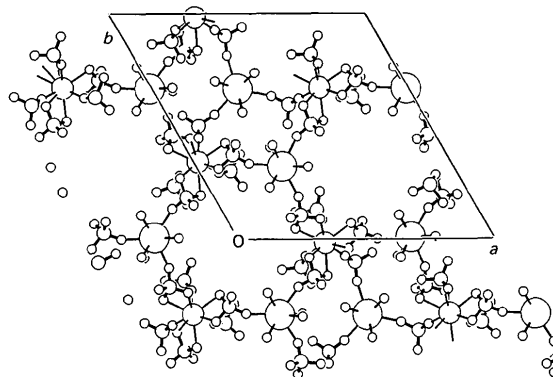

Fig. 1. View down c of the layer $0.0 < z < 0.5$ of the title compound. In order of decreasing size the atoms are Nd^{III}, Ce^{IV}, S and O. Coordinated water molecules are included but the lattice water is omitted.

Fig. 2. Schematic representation of the coordination of the Ce and Nd atoms, drawn perpendicular to c. Metal atoms on the right-hand side lie close to an arc of radius $a/3$ about the $(0, \frac{1}{3}, z)$ position of the left-hand Ce3 and Nd1 atoms. z coordinates ($\times 10^3$) are given in parentheses.

Fig. 3. Coordination of the $Ce_2(SO_4)_9^{10-}$ anion, with sulfate bridges to Nd1 and Nd2. Atoms carrying numerals only are oxygen.

are not bridged; the distance and geometry of the coordinated water molecules preclude even hydrogen bonding. In a recent study of $Cs_2Th(SO_4)_3.2H_2O$ (Habash & Smith, 1992), it was reported that there was a significant difference between the S—O distances for coordinated O (1.48 Å average) and for terminal O (1.43 Å average). The O—S—O angle was 103.1° (average) for chelated groups and 110.7° for the rest. In the present compound there is no significant difference between the average S—O(terminal) [1.456 (6) Å] and S—O(to Nd) [1.447 (6) Å] distances. The average S—O(bidentate to Ce) distance is 1.490 Å. S—O(monodentate to Ce) distances are spread widely [O13 1.482 (8), O23 1.467 (6) and O33 1.439 (6) Å]. Ignoring O33, which is part of an HSO_4^- group, S—O(cerium) distances are significantly longer than S—O(neodymium) distances. The average chelated O—S—O angle is 102.8°; the other O—S—O angles have an average value of 110.7°.

The short bridging Ce—O distances combined with longer S—O and the relatively long Nd—O distances suggest that the dimeric anion $Ce_2(SO_4)_9^{10-}$ is a significant chemical unit in the organization of the structure, although it is not as well defined as, for example, the $Ce_2(O_2)_2(CO_3)_8^{8-}$ dimer (Barnes & Blyth, 1985; Barnes, Blyth, Paton & Smith, 1990). The deeper colour noted for each of this series of Ln^{III}/Ce^{IV} compounds compared with $Ce(SO_4)_2.4H_2O$ probably involves a modification of the lowest lying O_n—Ce^{IV} transition in the change from $(4H_2O,4O$—$SO_3)$ in $Ce(SO_4)_2.4H_2O$ to $(9O$—$SO_3)$ in the present compound. Sulfate is a spectroscopically innocent ligand so that a charge-transfer transition between Ln^{III} and Ce^{IV} via sulfate seems unlikely.

Sites for the acid protons are not completely obvious. Only S30—O32 [1.605 (13) Å] falls in the range 1.54–1.61 Å associated with S—OH distances. Since O32 is in a special position $(6h)$, six protons in the cell are accounted for. $W2$ lies on a threefold axis and so is either an H_3O^+ group or an H_2O with rotational disorder. The remaining protons must be associated with the solvent water molecules, probably in a disordered arrangement.

The thermal parameters of the S30 hydrogen sulfate ion are relatively large and anisotropic. This group could be partially disordered but an attempt to refine a disordered model for O32 was not successful. The single bond S30—O32 [1.605 (13) Å] is accompanied by a shortening of the terminal S30—O31 [1.329 (13) Å] and S30—O33 links to Ce3 [1.439 (6) Å] compared with the corresponding bonds at S10 and S20. The average of S10—O11 and S20—O21 is 1.442 (8) Å and the average of S10—O13 and S20—O23 is 1.474 (8) Å.

Fig. 4 shows that the structure contains an open channel (5.1 Å diameter) at $(0, 0, z)$, which is continuous through the structure, and voids (approximately 5.1 Å diameter and 15 Å long) at $(\frac{1}{3}, \frac{2}{3}, z)$ and $(\frac{2}{3}, \frac{1}{3}, z)$. These voids are sealed by an Nd2 ion and its coordination environment,

once in the unit cell. Channels and voids are surrounded by sulfate O atoms and coordinated water molecules. The non-coordinated water molecules, $W1$-$W8$, which include disordered and partially occupied examples, are found in these channels. Apart from $W2$ (see above) the water molecules are held close to the edges of the channels by hydrogen bonds. This open channel structure explains the range of the early analyses. The water content can vary from crystal to crystal and extra sulfuric acid could be entrained.
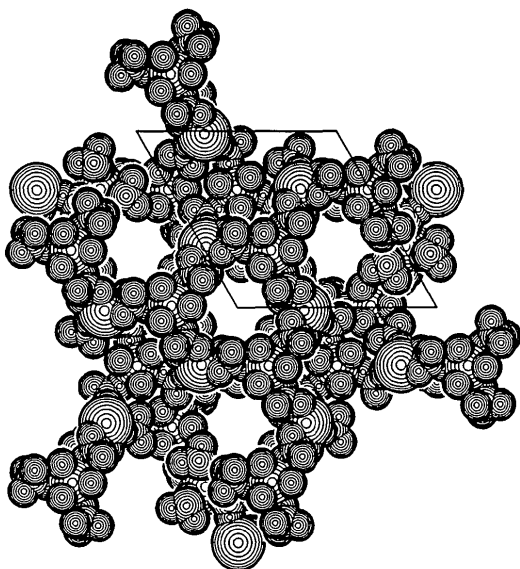
Fig. 4. View down c, using CPK radii to show the infinite channels at $(0, 0, z)$ and the void at ($\frac{2}{3}$, $\frac{1}{3}$, 0). In the layer shown the corresponding void at ($\frac{1}{3}$, $\frac{2}{3}$, 0) is blocked by Nd2 and the associated groups.

Experimental

Crystal data

$H_9Ce_6Nd_7(SO_4)_{27}.72.33H_2O$
M_r = 5756.07
Hexagonal
$P6_3/m$
a = 19.165 (3) Å
c = 25.060 (4) Å
V = 7971.3 (22) Å^3
Z = 2
D_x = 2.400 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
μ = 4.410 mm^{-1}
T = 293 (2) K
Cell parameters from 250 reflections
Transparent hexagonal columns
0.6 × 0.4 × 0.4 mm
Greyish yellow

Data collection

Enraf-Nonius FAST four-circle diffractometer
Integration from area detector scans
Absorption correction:
  DIFABS (Walker & Stuart, 1983)
  T_{min} = 0.74, T_{max} = 0.91

22 395 measured reflections
4318 independent reflections
3500 observed reflections
  $[I > 2\sigma(I)]$
R_{int} = 0.0379
θ_{max} = 24.82°
h = -21 → 15
k = -16 → 22
l = -27 → 28

Refinement

Refinement on F^2
$R(F)$ = 0.0378
$wR(F^2)$ = 0.1156
S = 0.598
4309 reflections
351 parameters
Calculated weights
  $w = 1/[\sigma^2(F_o^2) + (0.0978P)^2 + 185.6694P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{max}$ = 2.592 e Å^{-3}
$\Delta\rho_{min}$ = -1.750 e Å^{-3}
Extinction correction:
  $F_c^* = kF_c[1 + 0.001F_c^2 \times \lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0
Atomic scattering factors from International Tables for X-ray Crystallography (1992, Vol C, Tables 4.2.6.8 and 6.1.1.4)

Data collection: FAST *MADNESS* (Enraf-Nonius, 1990). Standard reflections not applicable for area-detector data collection. Cell refinement: FAST *MADNESS*. Data reduction: FAST *MADNESS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1993). Refinement was on F^2 for all reflections except for nine with very negative F^2 or flagged by the user for potential systematic errors. Molecular graphics: *PLUTON*92 (Spek, 1992). Software used to prepare material for publication: *SHELXL*92.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i.a_j.$$

	x	y	z	U_{eq}
Nd1	0.33318 (2)	0.32349 (3)	0.39326 (2)	0.0087 (2)
Nd2	0.3333	0.6667	0.2500	0.0117 (3)
Ce3	0.01604 (3)	0.34500 (3)	0.35551 (2)	0.0080 (2)
S10	0.1224 (2)	0.3037 (2)	0.2500	0.0086 (6)
S20	0.5970 (2)	0.0997 (2)	0.7500	0.0086 (6)
S30	0.3702 (3)	0.1310 (2)	0.2500	0.0482 (13)
S40	0.18814 (11)	0.29656 (12)	0.91136 (8)	0.0104 (4)
S50	0.96926 (13)	0.46036 (12)	0.09367 (8)	0.0161 (5)
S60	0.20902 (12)	0.83297 (12)	0.41598 (8)	0.0128 (4)
O1	0.5642 (3)	0.2631 (4)	0.8207 (2)	0.0237 (14)
O2	0.3418 (4)	0.4168 (4)	0.4670 (2)	0.027 (2)
O3	0.3282 (3)	0.4091 (4)	0.3205 (2)	0.0210 (14)
O4	0.2373 (4)	0.2295 (3)	0.4604 (2)	0.0214 (14)
O5	0.4344 (4)	0.3235 (3)	0.4560 (2)	0.0232 (14)
O6	0.4280 (4)	0.3191 (4)	0.3269 (2)	0.0263 (15)
O7	0.2368 (4)	0.2266 (4)	0.3261 (3)	0.034 (2)
O11	0.1969 (5)	0.3791 (5)	0.2500	0.016 (2)
O12	0.1353 (5)	0.2353 (5)	0.2500	0.022 (2)
O13	0.0731 (3)	0.2961 (3)	0.2976 (2)	0.0215 (14)
O21	0.1864 (5)	0.5532 (5)	0.2500	0.031 (2)
O22	0.0599 (5)	0.5501 (5)	0.2500	0.015 (2)
O23	0.0733 (4)	0.4505 (4)	0.2972 (2)	0.0265 (15)
O31	-0.2104 (7)	0.2083 (9)	0.2500	0.091 (5)
O32	-0.1225 (9)	0.1600 (7)	0.2500	0.088 (5)
O33	-0.0874 (4)	0.2837 (4)	0.2965 (2)	0.031 (2)
O41	-0.0970 (3)	0.1553 (3)	0.4607 (2)	0.0208 (14)
O42	-0.1898 (3)	0.1387 (3)	0.3914 (2)	0.0166 (13)
O43	-0.0901 (3)	0.2727 (3)	0.4192 (2)	0.0145 (12)
O44	-0.0473 (4)	0.1975 (4)	0.3711 (2)	0.0218 (14)
O51	0.5578 (4)	0.4766 (4)	0.4537 (3)	0.035 (2)
O52	0.4583 (4)	0.4562 (3)	0.3885 (2)	0.0178 (13)
O53	0.0393 (3)	0.4484 (3)	0.4182 (2)	0.0190 (13)
O54	-0.0725 (4)	0.4030 (4)	0.3620 (2)	0.0214 (14)
O61	0.2019 (3)	0.4220 (4)	0.4647 (2)	0.0228 (14)
O62	0.2108 (3)	0.3367 (4)	0.3983 (2)	0.0173 (13)
O63	0.0807 (3)	0.3141 (3)	0.4244 (2)	0.0178 (13)
O64	0.1629 (3)	0.4273 (3)	0.3728 (2)	0.0152 (13)
OW1	0.5315 (7)	0.4262 (7)	0.2500	0.054 (3)
OW2	0.0000	0.0000	0.1568 (7)	0.071 (5)
OW3	0.1512 (5)	0.0820 (5)	0.9186 (5)	0.086 (4)
OW4A	0.0824 (10)	0.1474 (10)	0.8039 (6)	0.051 (4)

OW4B	0.1143 (10)	0.1233 (10)	0.8006 (6)	0.047 (4)
OW5	0.5790 (4)	0.1825 (4)	0.9109 (3)	0.038 (2)
OW6	−0.2401 (8)	0.2781 (8)	0.3934 (5)	0.086 (6)
OW7	0.6124 (20)	0.2489 (21)	1.0001 (14)	0.054 (14)
OW8	0.0485 (22)	−0.0258 (22)	0.9713 (14)	0.016 (13)

Table 2. *Selected geometric parameters* (Å)

Nd1—O4	2.478 (6)	S10—O13^{iii}	1.482 (6)
Nd1—O52	2.477 (6)	S20—O22^{iv}	1.447 (8)
Nd1—O62	2.484 (5)	S20—O21^{iv}	1.445 (9)
Nd1—O3	2.487 (6)	S20—O23^{v}	1.467 (6)
Nd1—O6	2.495 (6)	S20—O23^{iv}	1.467 (6)
Nd1—O5	2.498 (6)	S30—O31^{i}	1.329 (13)
Nd1—O7	2.503 (6)	S30—O33^{i}	1.439 (6)
Nd1—O2	2.520 (6)	S30—O33^{vi}	1.439 (6)
Nd1—O42^{i}	2.520 (5)	S30—O32^{i}	1.605 (13)
Nd2—O1^{ii}	2.483 (6)	S40—O42^{vii}	1.449 (6)
Ce3—O33	2.273 (6)	S40—O41^{vii}	1.453 (6)
Ce3—O13	2.283 (6)	S40—O44^{vii}	1.486 (6)
Ce3—O23	2.282 (6)	S40—O43^{vii}	1.490 (6)
Ce3—O63	2.366 (5)	S50—O52^{viii}	1.441 (6)
Ce3—O53	2.390 (6)	S50—O51^{viii}	1.459 (6)
Ce3—O43	2.405 (5)	S50—O54^{ix}	1.485 (6)
Ce3—O54	2.454 (6)	S50—O53^{ix}	1.499 (6)
Ce3—O64	2.482 (6)	S60—O62^{x}	1.451 (6)
Ce3—O44	2.487 (6)	S60—O61^{x}	1.456 (6)
S10—O11	1.437 (8)	S60—O64^{x}	1.489 (6)
S10—O12	1.452 (9)	S60—O63^{x}	1.493 (6)
S10—O13	1.482 (6)		

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

Evaporation at room temperature of a solution of $Nd_2(SO_4)_3.5H_2O$ and $Ce(SO_4)_2.4H_2O$ in $2M$ H_2SO_4 gave a mixture of yellow $Ce(SO_4)_2.4H_2O$ crystals and hexagonal columnar greyish yellow crystals of the product. The latter kept indefinitely under the mother liquor but lost water in air. Data were collected and the unit cell refined on the SERC Enraf–Nonius FAST diffractometer at Cardiff University, using graphite-monochromated Mo radiation. Scattering factors, dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C). The structure was solved in space group $P\bar{1}$ and extended to show all the metal and S atoms and 105 unique O atoms ($R = 0.11$). At this stage the relationship to the true hexagonal cell and the correct space group, $P6_3/m$, became apparent.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71417 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1068]

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Structure Determination of SnZrS3

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Abstract

The structure of tin zirconium trisulfide is of the NH_4CdCl_3 type with double columns of edge-sharing Zr octahedra. These columns are linked together by Sn atoms. Sn is coordinated to three S atoms at 2×2.619 (2) and 2.765 (2) Å; a fourth S atom is at 3.065 (2) Å. The zirconium coordination is approximately octahedral with six S atoms at 2.524 (2), 2×2.545 (2), 2.582 (2) and 2×2.592 (2) Å. Powder diffraction data were also collected; the JCPDS File No. for tin zirconium sulfide is 44-1494.

Comment

A number of ternary chalcogenides ABX_3 (X = S, Se) occur in the NH_4CdCl_3 structure type characterized by double columns of edge-sharing octahedra of B, linked together by A. This is found for $PbZrS_3$ (Lelieveld & IJdo, 1978), $SnHfS_3$ and $PbHfS_3$ (Wiegers, Meetsma, Haange & de Boer, 1989), where Zr and Hf are in octahedra of S atoms, for the mixed-valence compound Sn_2S_3 (Mootz & Puhl, 1967; Jumas, Ribes, Philippott & Maurin, 1972; Yamaoka & Okai, 1970), and for the selenides $LaCrSe_3$ (Huy-Dung, Etienne & Laruelle, 1971)