Data collection

Philips PW1100 diffractom-
eter
ω–2θ scans
Absorption correction:
analytical by integration
from crystal shape
$T_{min} = 0.095$, $T_{max} =$
0.646
968 measured reflections
243 independent reflections

176 observed reflections
$[F > 3\sigma(F)]$
$R_{int} = 0.137$
$\theta_{max} = 29.94°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 23$
2 standard reflections
frequency: 60 min
intensity decay: 0.8 and
1.87%

Refinement

Refinement on F
$R = 0.066$
$wR = 0.034$
$S = 2.512$
170 reflections
18 parameters
Weighting scheme based
on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.0007$
$\Delta\rho_{max} = 3.28$ e Å^{-3}
$\Delta\rho_{min} = -4.06$ e Å^{-3}

Extinction correction:
Zachariasen (1968)
Extinction coefficient:
500.00
Atomic scattering factors
from *International Tables
for X-ray Crystallography*
(1974, Vol. IV, Tables
2.2B and 2.3.1)

Table 3. *Fractional atomic coordinates and equivalent
isotropic displacement parameters* (Å²) *for* CeNi₂Zn

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

		x	y	z	U_{eq}
Ce1	4(*f*)	1/3	2/3	0.53984 (7)	0.0132 (4)
Ce2	2(*d*)	1/3	2/3	3/4	0.0215 (7)
Ni	12(*k*)	0.1674 (3)	2*x*	0.12571 (7)	0.0093 (6)
Zn1	2(*c*)	1/3	2/3	1/4	0.020 (1)
Zn2	2(*b*)	0	0	1/4	0.016 (1)
Zn3	2(*a*)	0	0	0	0.012 (1)

Table 4. *Interatomic distances up to 4 Å in* CeNi₂Zn

Ce1		Ce2	
—Ni	2.890 (4) ×6	—Zn1	2.912 (1) ×3
—Zn3	2.985 (1) ×3	—Zn2	2.912 (1) ×3
—Ni	3.083 (2) ×3	—Ni	3.246 (4) ×12
—Ce1	3.193 (1) ×3	—Ce1	3.454 (2) ×2
—Ce1	3.454 (2)		

Ni		Zn1	
—Zn1	2.505 (2)	—Ni	2.505 (2) ×6
—Zn2	2.512 (2)	—Ce2	2.912 (1) ×2
—Ni	2.512 (3) ×2	—Zn2	2.912 (1) ×3
—Zn3	2.531 (2)	—Ce2	2.9132 (9)
—Ni	2.533 (4) ×2		
—Ce1	2.890 (4) ×2		
—Ce1	3.083 (2)		
—Ce2	3.246 (4) ×2		

Zn2		Zn3	
—Ni	2.512 (2) ×6	—Ni	2.531 (2) ×6
—Zn1	2.912 (1) ×3	—Ce1	2.985 (1) ×6
—Ce2	2.912 (1) ×3		

The *Xtal*3.2 package (Hall, Flack & Stewart, 1992) was used
for cell refinement and data reduction. Structure solution was
by *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate &
Woolfson, 1987). *Xtal*3.2 was used for least-squares refinement
based on |F| values, varying a scale factor, isotropic extinction,
atomic positional and anisotropic displacement parameters.

The absorption correction was performed using *LSABS* (Blanc,
Schwarzenbach & Flack, 1991). The atomic coordinates were
standardized by *STRUCTURE TIDY* (Gelato & Parthé, 1987)

Lists of structure factors, anisotropic displacement parameters and
complete geometry have been deposited with the IUCr (Reference:
DU1126). Copies may be obtained through The Managing Editor,
International Union of Crystallography, 5 Abbey Square, Chester CH1
2HU, England.

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An Acid Terbium(III) Cerium(IV) Sulfate Hydrate, H₉Tb₇Ce₆(SO₄)₂₇.72.2H₂O

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Abstract

Hexagonal crystals of H₉Ln₇Ce₆(SO₄)₂₇.72H₂O are
known for Ln = La–Tb. The Tb compound is iso-
morphous with the Nd compound described previously.
Tb—O (2.55 Å average) is unusually long compared
with a typical literature value of 2.43 Å and, in spite
of the lanthanide contraction, is longer than the corre-
sponding Nd—O distance although the Ce—O distances
are identical. Since the quality of the crystals and hence
the data is not as good for the Tb compound, and since
this phase has not been reported for Ln = Dy–Lu, it
may be that the size of the Ln^{III} site is fixed by the
Ce^{IV}–SO$_4^{2-}$ network.

Comment

Brauner (1904) reported hexagonal acid sulfato complexes containing both Ln^{III} (La–Nd) and Ce^{IV}. Barnes, Paton & Seaward (1993) reported the structure of one compound of this series, $H_9Nd_7Ce_6(SO_4)_{27}.72.33H_2O$, (I). Although extension of the series beyond Nd proved difficult, some crystals of the Tb^{III} analogue, (II), were obtained. Whereas (I) refined to $R = 0.038$, refinement of the Tb structure has been less satisfactory. Data were collected from two crystals, one at 150 K and the other at 120 K, using an Enraf–Nonius FAST area-detector diffractometer. In each case, the mosaic spread was large and reflections were hard to centre. The unit cells obtained differ by 4σ in a, but by over 30σ in c. Tables of atomic coordinates and interatomic distances given below are derived from the 120 K data, which refined anisotropically to $R = 0.069$ for 4380 data. No atom gave 'non-positive definite' atomic displacement parameters. In contrast, the 150 K data gave no satisfactory anisotropic refinement. Isotropic refinement converged at $R = 0.071$ for 3430 data with $F_o > 4\sigma(F_o)$. The difference between the two data sets is felt to reflect the quality of the individual crystals; no significant difference in structure was detected.

The architecture (Fig. 1) is the same as in the Nd compound (see figures in Barnes, Paton & Seaward, 1993). The two unique Tb environments and the Ce environments are each made up of nine O atoms from water or sulfate groups, giving tricapped trigonal prismatic coordination. The structure extends through sulfate bridges to form layers perpendicular to the c-axis direction and $1/2c$ (ca 12.5 Å) thick. Uncoordinated solvent water is located in open channels 5.1 Å in diameter parallel to c at $0,0,z$, and similar channels at $2/3,1/3,z$ and $1/3,2/3,z$, which are blocked once in each unit cell. The solvent water content can vary from crystal to crystal and between cells within the crystal. The positions and site occupancies reported for these water molecules indicate features which remained stable over successive stages of refinement. There may well be other partially occupied water sites concealed by the noise level on the final difference maps [about $2.5\,e\,\text{Å}^{-3}$ for both (I) and (II)]. Most of the nine protons required by charge balance must be associated with water molecules.

In (I), the average Nd—O and Ce—O distances (Nd1—O 2.496, Nd2—O 2.507, Ce3—O 2.380 Å) are typical of literature values. The lanthanide contraction suggests that Tb—O should be shorter than Nd—O. The average Tb—O distance over a selection of compounds from the Cambridge Structural Database (Allen $et\ al.$, 1987) is 2.426 Å. However, both crystals of (II) have average Tb—O distances longer than the average Nd—O distance in (I), although the Ce—O distances are very similar in (I) and (II). At 120 K the average distances are Tb1—O 2.538, Tb2—O 2.564 and Ce3—O 2.407 Å, and at 150 K the average distances are Tb1—O 2.514, Tb2—O 2.543 and Ce3—O 2.381 Å. The variation of the Tb—O distances in the structure is within 0.06 Å, whereas variations of up to 0.25 Å are not uncommon in the literature.

These observations may be explained if the dimensions of the layer are largely controlled by the Ce^{IV}–SO_4^{2-} framework. Coulombic interactions of Ce^{4+} will be significantly greater than those of Ln^{3+}. In this situation the Ln^{III}—O distance could be dictated by the framework rather than by the conventional ionic radii. This is consistent with the greater stability, better crystal quality and better defined structure of the Nd compound (I) compared with (II) containing the smaller Tb ion, and with the failure to produce this phase for the elements beyond Tb. The variation in c for the different crystals of (II) may correlate with changes in solvent water content altering the length of the channels and pushing the layers apart. Water was detected on eight sites in the 150 K Tb crystal and on nine sites in the 120 K crystal for which c was significantly greater.
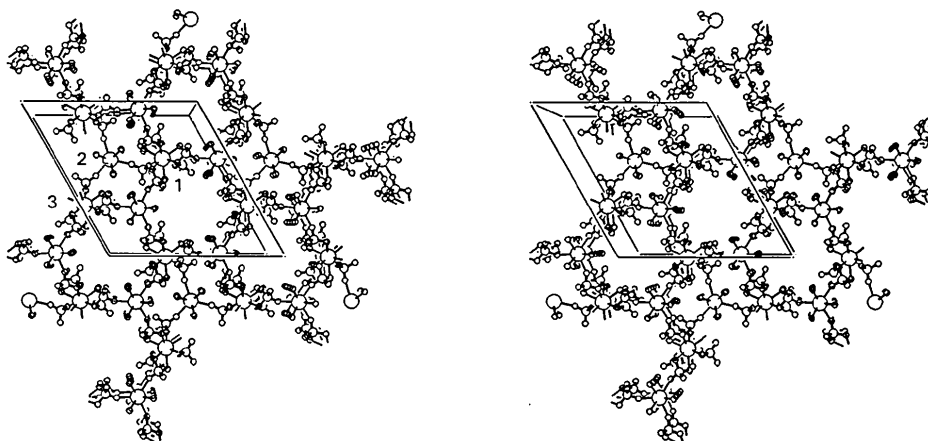

Fig. 1. Stereoview down c showing the $Tb_7Ce_6(SO_4)_{27}(H_2O)_{42}$ framework. The lanthanide atoms are: 1, Tb1; 2, Tb2; 3, Ce3.

All the sulfate groups in (I) and (II), except that at S30, give small anisotropic displacement parameters, S—O distances of 1.43–1.51 Å and O—S—O angles of 106–112°. In both structures S30, O31 and O32 are disordered over at least two positions whereas O33 is fixed by coordination to Ce3. The disorder is seen in the short S30—O31 distance, apparently only 1.24 (2) Å, and in the ellipsoids of S30 and O31 (Fig. 2), which are related and show gross elongation perpendicular to the plane of S30, O33 and O33′. The principal mean-square displacements in (II) are 0.1551, 0.0127, 0.0035 (S30) and 0.3446, 0.0374, 0.0115 (O31). O32 appears as an exaggerated disc perpendicular to the vector S30—O32, with S30—O32 1.58 (2) Å. (principal mean-square displacements 0.1652, 0.0824, 0.0015). It is possible that one position of S30 and O31 is associated with a protonated O32 and a true S30—O32 bond of about 1.65 Å, and another position with the absence of this proton reducing the distance to about 1.48 Å. An attempt to explore this disorder in (I) gave no satisfactory model.
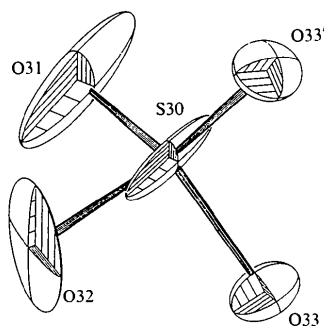

Fig. 2. Apparent displacement ellipsoids (50% probability) for the disordered sulfate ion at S30.

In (II), the Tb1 and Ce3 sites have significant residual electron density at convergence (4.4 and $6.3 \, e \, Å^{-3}$, respectively). Similar features can be obtained from the 150 K data, but are not seen in (I). Partial occupancy of the Ce3 site by Tb seems unlikely. Tb^{3+} is too big for the Ce^{4+} site and oxidation to Tb^{4+} is improbable in an aqueous medium ($E_0 \simeq 2.8$ V). The features are probably only another sign of the lower crystal quality of (II) compared with (I).

Experimental

The terbium compound was prepared by the same route as the neodymium and cerium(III) analogues (Barnes, Paton & Seaward, 1993). Individual darker hexagonal prisms containing Tb^{III} and Ce^{IV} were selected from the yellow mass of recrystallized ceric sulfate. The crystals lose water slowly in air but can be kept indefinitely under the mother liquor. Samples for diffractometry were mounted in oil drops before cooling to 120 or 150 K.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *at* 120 K

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

	x	y	z	U_{eq}
Tb1	0.33255 (3)	0.32358 (4)	0.39311 (3)	0.0176 (2)
Tb2	1/3	2/3	1/4	0.0294 (4)
Ce3	0.01560 (4)	0.34501 (4)	0.35526 (3)	0.0080 (2)
S10	0.1218 (2)	0.3040 (2)	1/4	0.0094 (8)
S20	0.5968 (2)	0.0990 (2)	3/4	0.0096 (8)
S30	0.3716 (5)	0.1313 (3)	1/4	0.058 (2)
S40	0.1885 (2)	0.2966 (2)	0.91119 (11)	0.0110 (6)
S50	0.9695 (2)	0.4603 (2)	0.09356 (11)	0.0155 (7)
S60	0.2102 (2)	0.8337 (2)	0.41585 (11)	0.0129 (6)
O1	0.5638 (6)	0.2637 (6)	0.8217 (4)	0.032 (2)
O2	0.3421 (5)	0.4168 (6)	0.4671 (3)	0.034 (3)
O3	0.3274 (5)	0.4089 (5)	0.3201 (3)	0.023 (2)
O4	0.2364 (6)	0.2284 (5)	0.4600 (3)	0.024 (2)
O5	0.4343 (5)	0.3234 (5)	0.4563 (3)	0.025 (2)
O6	0.4277 (6)	0.3184 (6)	0.3269 (3)	0.031 (2)
O7	0.2346 (6)	0.2268 (6)	0.3259 (4)	0.039 (3)
O11	0.1962 (7)	0.3776 (7)	1/4	0.016 (2)
O12	0.1350 (7)	0.2349 (8)	1/4	0.025 (3)
O13	0.0727 (5)	0.2957 (5)	0.2976 (3)	0.021 (2)
O21	0.1861 (8)	0.5508 (8)	1/4	0.036 (4)
O22	0.0597 (7)	0.5502 (7)	1/4	0.017 (3)
O23	0.0722 (6)	0.4511 (6)	0.2973 (3)	0.028 (2)
O31	-0.2052 (12)	0.2064 (17)	1/4	0.135 (14)
O32	-0.1248 (14)	0.1622 (10)	1/4	0.087 (7)
O33	-0.0871 (6)	0.2846 (6)	0.2968 (3)	0.030 (2)
O41	-0.0959 (5)	0.1560 (5)	0.4606 (3)	0.022 (2)
O42	-0.1889 (5)	0.1393 (5)	0.3913 (3)	0.020 (2)
O43	-0.0903 (5)	0.2734 (5)	0.4193 (3)	0.017 (2)
O44	-0.0462 (5)	0.1992 (5)	0.3704 (3)	0.019 (2)

O51	0.5582 (6)	0.4765 (5)	0.4534 (3)	0.031 (2)
O52	0.4575 (5)	0.4567 (5)	0.3887 (3)	0.024 (2)
O53	0.0392 (5)	0.4479 (5)	0.4183 (3)	0.021 (2)
O54	−0.0722 (5)	0.4029 (5)	0.3621 (3)	0.020 (2)
O61	0.2015 (5)	0.4232 (5)	0.4644 (3)	0.023 (2)
O62	0.2101 (5)	0.3365 (5)	0.3989 (3)	0.019 (2)
O63	0.0802 (5)	0.3143 (5)	0.4243 (3)	0.017 (2)
O64	0.1628 (5)	0.4276 (5)	0.3729 (3)	0.017 (2)
O1W	0.5291 (10)	0.4235 (10)	1/4	0.050 (4)
O2W	0	0	0.1568 (11)	0.082 (8)
O3W	0.1497 (7)	0.0837 (8)	0.9203 (7)	0.087 (5)
O4WA	0.0825 (14)	0.1478 (14)	0.8048 (8)	0.046 (6)
O4WB	0.1141 (17)	0.1205 (18)	0.8006 (10)	0.066 (7)
O5W	0.5807 (7)	0.1833 (7)	0.9102 (5)	0.051 (3)
O6W	−0.2386 (16)	0.2775 (16)	0.3971 (10)	0.116 (12)
O7W	2/3	1/3	0.981 (2)	0.37 (5)
O8W	0.047 (3)	−0.026 (3)	0.9702 (19)	0.025 (19)

Table 2. *Selected geometric parameters* (Å)

Tb1—O52	2.502 (11)	S10—O12	1.480 (14)
Tb1—O62	2.507 (10)	S10—O13^{iii}	1.507 (8)
Tb1—O4	2.525 (9)	S20—O21^{iv}	1.462 (14)
Tb1—O3	2.532 (8)	S20—O22^{iv}	1.465 (13)
Tb1—O6	2.544 (10)	S20—O23^{iv}	1.486 (9)
Tb1—O5	2.553 (9)	S30—O31^{i}	1.24 (2)
Tb1—O7	2.555 (10)	S30—O33^{v}	1.475 (9)
Tb1—O2	2.562 (9)	S30—O32^{i}	1.58 (2)
Tb1—O42^{i}	2.565 (10)	S40—O42^{vi}	1.457 (9)
Tb2—O1^{ii}	2.547 (10)	S40—O41^{vi}	1.486 (9)
Tb2—O21	2.598 (14)	S40—O43^{vi}	1.513 (10)
Ce3—O33	2.291 (9)	S40—O44^{vi}	1.524 (8)
Ce3—O13	2.319 (8)	S50—O52^{vii}	1.467 (10)
Ce3—O23	2.320 (9)	S50—O51^{vii}	1.487 (9)
Ce3—O63	2.407 (8)	S50—O54^{viii}	1.512 (9)
Ce3—O53	2.424 (9)	S50—O53^{viii}	1.515 (10)
Ce3—O43	2.446 (8)	S60—O62^{ix}	1.470 (9)
Ce3—O54	2.465 (10)	S60—O61^{ix}	1.491 (9)
Ce3—O44	2.482 (10)	S60—O63^{ix}	1.505 (9)
Ce3—O64	2.513 (10)	S60—O64^{ix}	1.505 (8)
S10—O11	1.431 (12)		

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

An area-detector system was used for data collection. Cell dimensions were refined from 250 reflections selected from two regions 90° apart and 5° wide at $\kappa = 0°$. Intensity standards were not measured by the area detector. Possible variations were checked by comparing intensities of common or symmetry-related reflections as they occurred during data collection. In this case no variation was noted.

Data collection: *FAST-MADNESS* (Enraf–Nonius, 1990). Cell refinement: *FAST-MADNESS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Monoclinic Mg2B2O5

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Abstract

The title monoclinic magnesium pyroborate was synthesized by solid-state reaction and its crystal structure determined by X-ray diffraction techniques. The structure is built from tetrameric chains of *trans*-edge-shared Mg octahedra (Mg_4O_{18}), held together by B atoms which form B_2O_5 (double-triangle) groups. The monoclinic and triclinic forms of $Mg_2B_2O_5$ are heteromorphic.

Comment

The MgO–B_2O_3 system has been studied extensively (Toropov & Konovalov, 1940; Davis & Knight, 1945; Block, Burley, Perloff & Mason, 1959; Nefedov, 1961; Kuzel, 1964; Mutluer & Timucin, 1975). Takeuchi (1952) has described the crystal structure of the monoclinic mineral suanite from the Suan mine, North Korea. Mrose & Fleischer (1963) studied and compared X-ray diffraction data of the monoclinic and triclinic forms of $Mg_2B_2O_5$. A recent paper by us (Guo, Cheng, Chen, Huang & Zhang, 1995) describes the crystal structure of triclinic $Mg_2B_2O_5$. In this work, we report the synthesis and crystal structure of the monoclinic form of $Mg_2B_2O_5$.

The monoclinic and triclinic forms of $Mg_2B_2O_5$ are heteromorphic. Fig. 1 shows the structure of monoclinic $Mg_2B_2O_5$. The structure of the monoclinic form of $Mg_2B_2O_5$ is based on Mg_4O_{18} tetramers, composed of four Mg octahedra linked by three shared edges, and connected by sharing four O···O edges to form