inorganic papers

Yttrium(III) sulfate octahydrate

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(S–O) = 0.003 Å
R factor = 0.040
wR factor = 0.095
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $Y_2(SO_4)_3 \cdot 8H_2O$, consists of infinite layers parallel to (10$\bar{1}$), with $[Y(H_2O)_4(SO_4)_{3/2}]$ as the unique repeat unit. The layers are linked only by hydrogen bonds of medium strength. The trivalent yttrium cation is coordinated by eight O atoms from four sulfate groups and four water molecules, in the form of a distorted square antiprism $[YO_8]$. The title compound is isostructural with the well known members of the rare-earth sulfate octahydrate structure type.

Comment

Most of the octahydrates of the rare-earth sulfates $[M_2(SO_4)_3 \cdot 8H_2O]$ have been structurally characterized in the last two decades. The temporary interest in the compounds was inspired by an erroneous structure determination of $Pr_2(SO_4)_3 \cdot 8H_2O$ in the non-centrosymmetric space group Cc, accompanied by the supposed existence of pyroelectricity in the crystals (Sherry, 1976). About the same time, structure analyses of $Sm_2(SO_4)_3 \cdot 8H_2O$ (Podberezskaya & Borisov, 1976), $Yb_2(SO_4)_3 \cdot 8H_2O$ (Hiltunen & Niinistö, 1976) and $Nd_2(SO_4)_3 \cdot 8H_2O$ (Bartl & Rodek, 1983) showed that the octahydrates belong to one structure type, which crystallizes in the centrosymmetric space group $C2/c$. Ahmed Farag *et al.* (1981) redetermined the structure of $Pr_2(SO_4)_3 \cdot 8H_2O$ and validated the isostructurality of this compound with the members of the octahydrate series. Recently, structure deter-
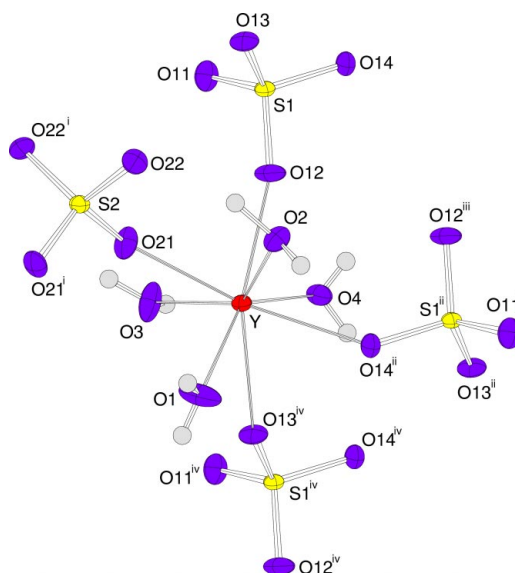

Figure 1
Clinographic *ORTEP*III (Burnett & Johnson, 1996) projection of the title compound, with the atom-numbering scheme. Non-H atoms are drawn as 50% probability ellipsoids and H atoms as spheres of arbitrary radius (symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $x, \frac{1}{2} - y, -z$; (iv) $x, y - 1, z$).
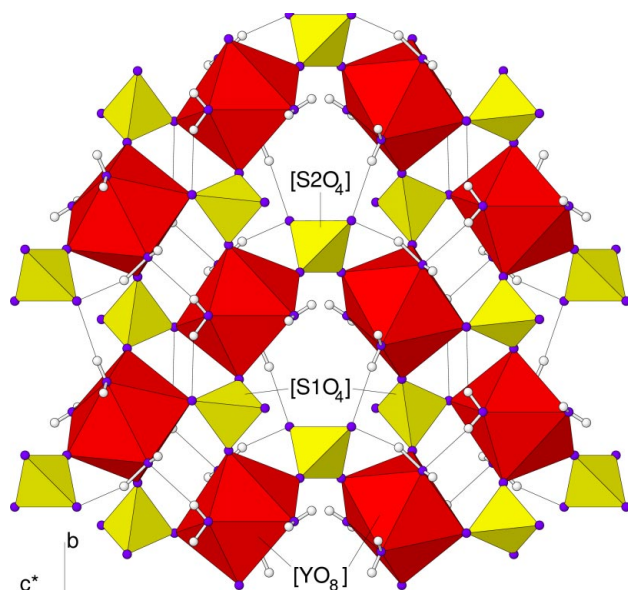
Figure 2
View perpendicular to the $(10\bar{1})$ layer of the title compound, with $[Y(H_2O)_{4/1}(SO_4(1))_{3/3}(SO_4(2))_{1/2}]$ as the repeat unit. Key: $[SO_4]$ tetrahedra (yellow), $[YO_8]$ antiprisms (red), oxygen (blue) and hydrogen (light grey) atoms.

minations of the Ce, Dy and Lu (Junk *et al.*, 1999) and Er (Wickleder, 1999) compounds expanded the structurally established octahydrate series. Wickleder (2002) has given a summary of all known hydrated rare-earth sulfates. In this paper we present one missing member of this structure type, *viz.* $Y_2(SO_4)_3 \cdot 8H_2O$, (I).

Although the calculated bond-valence sum points to a sevenfold coordination (2.969 v.u. up to O4, see Table 1), trivalent yttrium is surrounded by eight O atoms in the range 2.275 (3) to 2.468 (3) Å [d_{mean} = 2.36 (7) Å, 3.267 v.u.] in the form of a distorted square antiprism $[YO_8]$. Four O atoms belong to monodentate sulfate groups, the remaining O atoms are water molecules (Fig. 1). Both symmetrically non-equivalent sulfate groups differ in their bridging function. In sulfate group $(S1O_4)^{2-}$, the O atoms O12, O13 and O14 are linked to three Y^{3+} cations, while $(S2O_4)^{2-}$ connects only two Y^{3+} cations (2 × O21) (Fig. 2). The yttrium coordination can be written as $Y(H_2O)_4(S1O_4)_3(S2O_4)$. The remaining O atoms (O11 and O22) of both sulfate groups serve as acceptor atoms of hydrogen bonds. The tetrahedral configuration of the sulfate atoms is almost ideal, with one exception. As O14 of $S1O_4$ takes part not only in yttrium coordination, but also in hydrogen-bond formation, the bonds O14 forms are weaker than those formed by other O atoms. As a result, the S—O bond distance is elongated. Notwithstanding, all calculated distances and angles fit well into the ranges found for many other structures.

Sulfate groups of first type, alternating with $[YO_8]$ antiprisms, build chains parallel to the *b* axis, sharing common O atoms. Two chains form a strand with opposite stave ends of different kinds, $[SO_4]$ and $[YO_8]$ respectively. In the strand, the yttrium cations are separated by a distance of 5.1322 (9) Å. With sulfur atom S2 lying on the special Wykoff site 4*e*, the

$S2O_4$ sulfate groups link the double chains into infinite layers parallel to $(10\bar{1})$ (Fig. 3). Hence the repeat identical unit of the layer has to be written as $[Y(H_2O)_{4/1}(S1O_4)_{3/3}(S2O_4)_{1/2}]$. Hydrogen bonds of medium-to-weak strength, in the range 2.711 (5)–3.052 (5) Å, interconnect the layers into a three-dimensional framework. The reliability of the hydrogen-bonding data is restricted, because five out of eight hydrogen positions were restrained in bond length during the refinement calculation, though we found an analogous hydrogen-bonding system in known octahydrate rare-earth sulfate structures [*M* = Ce and Lu (Junk *et al.*, 1999), Nd (Bartl & Rodek, 1983) and Er (Wickleder, 1999)] in which the hydrogen positions had been determined experimentally.

Experimental

The crystallization of $Y_2(SO_4)_3 \cdot 8H_2O$ from an aqueous solution of sulfuric acid, yttrium sulfate and ethylenediamine in the molar ratio 1:1:1 was not expected (in our search for double sulfates of ethylenediammonium and trivalent cations). Heating, to 330 K, of the solution involved in the neutralization reaction of sulfuric acid and ethylenediamine is the key to the synthesis of the title compound. It crystallized by slow evaporation of the solvent at room temperature, in the form of colourless flat crystals with dimensions up to 5 mm.

Crystal data

$H_{16}O_{20}S_3Y_2$	D_x = 2.524 Mg m^{-3}
M_r = 610.11	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 25
a = 13.4802 (9) Å	reflections
b = 6.6846 (4) Å	θ = 12.5–17.4°
c = 18.2160 (10) Å	μ = 7.69 mm^{-1}
β = 101.977 (7)°	T = 293 (2) K
V = 1605.71 (17) Å^3	Parallelepiped, colourless
Z = 4	$0.25 \times 0.23 \times 0.19$ mm

Data collection

Nonius MACH3 diffractometer	R_{int} = 0.034
$\omega/2\theta$ scans	θ_{max} = 30.4°
Absorption correction: ψ scan	$h = -18 \rightarrow 19$
(*MolEN*; Fair, 1990)	$k = -9 \rightarrow 0$
T_{min} = 0.168, T_{max} = 0.232	$l = -25 \rightarrow 0$
2498 measured reflections	3 standard reflections
2424 independent reflections	frequency: 60 min
1614 reflections with $I > 2\sigma(I)$	intensity decay: 2.7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.095	$(\Delta/\sigma)_{max} < 0.001$
S = 1.06	$\Delta\rho_{max}$ = 0.94 e Å^{-3}
2424 reflections	$\Delta\rho_{min}$ = −0.87 e Å^{-3}
147 parameters	Extinction correction: *SHELXL*97
All H-atom parameters refined	(Sheldrick, 1997)
	Extinction coefficient: 0.0029 (2)

Table 1
Selected geometric parameters (Å).

Y1—O12	2.275 (3)	Y1—O2	2.468 (3)
Y1—O3	2.303 (3)	S1—O11	1.458 (3)
Y1—O21	2.302 (3)	S1—O12	1.463 (3)
Y1—O1	2.332 (4)	S1—O13	1.468 (3)
Y1—O13^{iv}	2.348 (3)	S1—O14	1.497 (3)
Y1—O14^{ii}	2.400 (3)	S2—O21	1.461 (3)
Y1—O4	2.416 (3)	S2—O22	1.475 (3)

Symmetry codes: (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iv) $x, y - 1, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

| $D—H \cdots A$	$D—H$	$H \cdots A$	$D \cdots A$	$D—H \cdots A$
O1—H11$\cdots$O22[iv]	0.74 (5)	2.10 (5)	2.837 (5)	172 (5)
O1—H12$\cdots$O11[v]	0.99 (5)	1.74 (5)	2.711 (5)	167 (7)
O2—H21$\cdots$O22	0.96 (5)	1.84 (5)	2.766 (5)	160 (7)
O2—H22$\cdots$O14[v]	0.82 (5)	2.28 (5)	3.052 (5)	156 (6)
O3—H31$\cdots$O11[vi]	0.80 (4)	2.07 (5)	2.765 (5)	146 (6)
O3—H32$\cdots$O22[vii]	0.89 (5)	1.95 (5)	2.812 (5)	163 (7)
O4—H41$\cdots$O2[ii]	0.72 (6)	2.26 (6)	2.968 (5)	168 (6)
O4—H42$\cdots$O14[iv]	0.79 (8)	2.11 (8)	2.809 (5)	147 (7)

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

Distance restraints were placed on O1—H12, O2—H21, O2—H22, O3—H31, O3—H32, with a target value of 0.98 (6) Å.

Data collection: *MACH*3 (Enraf–Nonius, 1993); cell refinement: *MACH*3; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 2002) and *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97.

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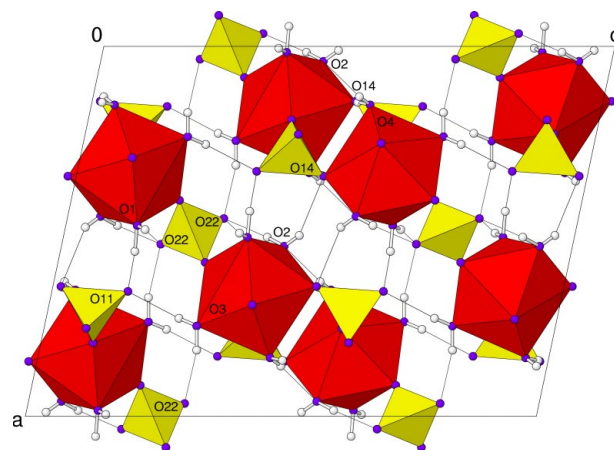
Figure 3
Projection of the title compound along [010]. Only hydrogen bonds (grey lines) interlink the layers parallel (10$\bar{1}$). (For the colour scheme, see Fig. 2)

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