Redeterminaton of the crystal structure of praseodymium sulfate octahydrate, $Pr_2(SO_4)_3 \cdot 8H_2O$

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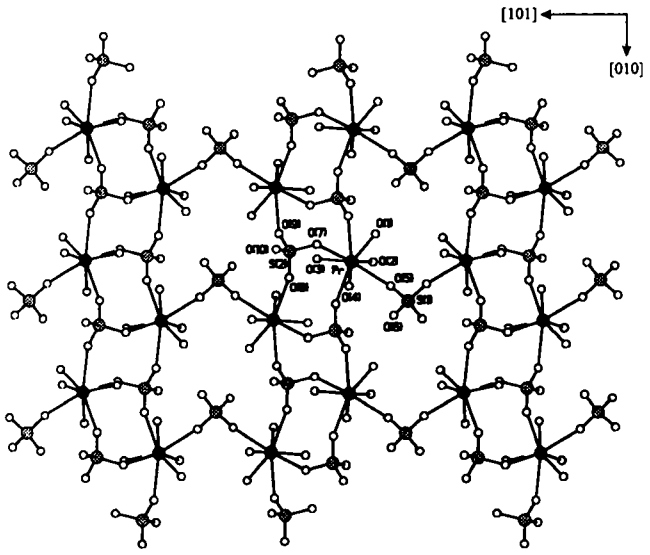

Abstract

$H_{16}O_{20}Pr_2S_3$, monoclinic, $C12/c1$ (No. 15), $a = 13.700(2)$ Å, $b = 6.861(1)$ Å, $c = 18.453(2)$ Å, $\beta = 102.80(1)°$, $V = 1691.4$ Å^3, $Z = 4$, $R_{gt}(F) = 0.023$, $wR_{ref}(F^2) = 0.060$, $T = 293$ K.

Source of material

Single crystal growth was optimized as follows. 0.10 g Pr_2O_3 was wetted with doubly distilled water and then a small amount of concentrated H_2SO_4 was dropwise added until the solid was completely disssolved. The resulting green solution was subsequently heated nearly to dryness. The obtained green crystalline substance was dissolved in 20 ml CH_3OH/H_2O (1:1 v/v) and 0.09 g 2,2′-bipyridine was added with stirring. The mixture was further stirred for one hour and then allowed to stand at room temperature. After three weeks, the pale green precipitate disappeared to give an orange solution. Green needle-like crystals were grown by slow evaporation at room temperature for another four weeks.

Discussion

The title sulfate $Pr_2(SO_4)_3 \cdot 8H_2O$ was reported to crystallize in the noncentrosymmetric space group Cc [1]. Our present redetermination based on more accurate single crystal X-ray diffraction data envidenced the correct space group to be the centrosymmetric one $C2/c$ (No. 15).

Within the title compound, the Pr atoms are each square antiprismatically coordinated by eight O atoms from four water molecules, one μ_2-SO_4^{2-} and three μ_3-SO_4^{2-} anions with d(Pr—O) = 2.392 Å – 2.568 Å. Actually, the water O atoms and the sulfato O atoms around the central Pr atom, respectively, occupy the corners of two interpenetrating tetrahedra. The bidentate sulfato group is crystallographically imposed by the C_2 symmetry with mean d(S(1)—O) = 1.467(2) Å and ∠O–S(1)–O = 109.0° – 111.1°, whereas the tridentate sulfato group with d(S(2)—O) = 1.454 Å – 1.499 Å and ∠O–S(2)–O = 106.9° – 111.9° exhibits significant deviation from the ideal T_d symmetry.

Along the [010] direction, the Pr atoms are bridged by tridentate sulfato groups into ribbon-like chains which are further bridged by bidentate sulfato groups along the [101] direction to form 2D $^2_\infty[Pr(H_2O)_4(\mu_2\text{-}SO_4\text{–}O,O')_{1/2}(\mu_3\text{-}SO_4\text{–}O,O',O'')_{3/3}]$ layers parallel to $(10\bar{1})$ with 8- and 16-membered rings. The water molecules donate hydrogen atoms to sulfato O atoms and water O atoms to form intra- and interlayer hydrogen bonds with d(O···O) = 2.736 Å – 2.988 Å and ∠O–H···O = 148° – 170°. The 2D layers are held together by the interlayer hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	pale green, pillar-like, size 0.156 × 0.156 × 0.467 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	61.62 cm^{-1}
Diffractometer, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2540, 1933
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1872
$N(param)_{refined}$:	147
Programs:	SHELXS-97 [2], SHELXL-97 [3]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
HA(O1)	8f	0.011(3)	–0.266(8)	0.343(2)	0.03(1)
HB(O1)	8f	–0.033(3)	–0.130(8)	0.354(3)	0.04(1)
HA(O2)	8f	0.234(7)	0.03(1)	0.253(5)	0.09(3)
HB(O2)	8f	0.320(5)	–0.029(7)	0.297(3)	0.04(1)
HA(O3)	8f	0.360(4)	–0.106(8)	0.481(3)	0.04(1)
HB(O3)	8f	0.383(4)	0.063(8)	0.483(3)	0.04(1)
HA(O4)	8f	0.015(4)	0.297(9)	0.408(3)	0.06(2)
HB(O4)	8f	–0.005(3)	0.188(8)	0.453(3)	0.05(1)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pr	8*f*	0.16920(1)	0.02570(3)	0.392779(8)	0.0197(2)	0.0150(2)	0.0184(1)	0.00150(5)	0.00430(8)	0.00118(5)
O(1)	8*f*	0.0141(2)	–0.1665(4)	0.3577(2)	0.023(1)	0.024(1)	0.068(2)	0.001(1)	–0.001(1)	–0.014(1)
O(2)	8*f*	0.2610(2)	–0.0008(5)	0.2955(2)	0.029(2)	0.064(2)	0.022(1)	0.018(1)	0.010(1)	0.008(1)
O(3)	8*f*	0.3499(2)	–0.0143(4)	0.4586(2)	0.027(1)	0.020(1)	0.026(1)	–0.0002(9)	0.001(1)	–0.002(1)
O(4)	8*f*	0.0385(2)	0.2380(4)	0.4360(1)	0.024(1)	0.027(1)	0.025(1)	0.004(1)	0.0062(9)	0.0030(9)
S(1)	4*e*	0	0.3291(2)	1/4	0.0200(4)	0.0175(5)	0.0175(4)	0	0.0025(3)	0
O(5)	8*f*	0.0838(2)	0.2059(4)	0.2866(1)	0.034(1)	0.037(1)	0.024(1)	0.017(1)	0.0068(9)	0.007(1)
O(6)	8*f*	–0.0319(2)	0.4502(4)	0.3062(1)	0.028(1)	0.027(1)	0.028(1)	0.001(1)	0.007(1)	–0.008(1)
S(2)	8*f*	0.21427(6)	–0.0319(1)	0.58866(4)	0.0208(4)	0.0148(4)	0.0175(3)	0.0009(2)	0.0048(3)	0.0001(2)
O(7)	8*f*	0.1423(2)	–0.0841(4)	0.5176(1)	0.029(1)	0.026(1)	0.0175(9)	0.001(1)	0.0008(8)	–0.0012(9)
O(8)	8*f*	0.2552(2)	0.1600(3)	0.5775(1)	0.036(1)	0.016(1)	0.048(1)	–0.0032(9)	0.010(1)	0.002(1)
O(9)	8*f*	0.2954(2)	–0.1759(3)	0.6032(1)	0.026(1)	0.020(1)	0.031(1)	0.0040(9)	0.0041(8)	–0.0011(9)
O(10)	8*f*	0.1611(2)	–0.0306(4)	0.6487(1)	0.029(1)	0.044(2)	0.021(1)	0.004(1)	0.009(1)	0.0010(9)

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