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The Structure of $Pr_2(SO_4)_3 \cdot 8H_2O$ and $La_2(SO_4)_3 \cdot 9H_2O$*

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The structures of $Pr_2(SO_4)_3 \cdot 8H_2O$ and $La_2(SO_4)_3 \cdot 9H_2O$ have been redetermined. The unit cell of $Pr_2(SO_4)_3 \cdot 8H_2O$ is monoclinic with $a = 13.675(3)$ Å, $b = 6.832(3)$ Å, $c = 18.426(3)$ Å, $\beta = 102.8(3)^\circ$, $Z = 4$, space group, $C_s{}^4 - Cc$. A least-squares refinement gave a final $R_f = 0.047$. The previously reported structure of $Nd_2(SO_4)_3 \cdot 8H_2O$ (all the rare-earth sulfates octahydrates are isomorphous) was incorrectly assigned to space group $C_{2h}^6 - C2/c$. This led to incorrect locations for the water molecules and an incorrect coordination number for the rare-earth ion of 9. In the present study, the coordination number of Pr is found to be 8. There are four sulfate and four water–oxygen atoms arranged in the form of a distorted Archimedian antiprism about the Pr atom. Each Pr is bonded to one oxygen from each of four sulfate groups. Two sulfate groups are bonded to three Pr's and the third sulfate group is bonded to two rare-earth atoms. Although hydrogen locations were not determined, there is evidence of hydrogen bonding between the SO_4–Pr–SO_4 chains. $La_2(SO_4)_3 \cdot 9H_2O$ is hexagonal with $a = 11.009(2)$ Å, $c = 8.076(20)$ Å, $Z = 2$, space group $C_{6h}^2 - P6_3/m$. A least-squares refinement gave a final $R_f = 0.063$. The La(2) is bonded to three oxygens from three sulfate groups and six water–oxygens. The second water molecule occupies holes in the structure.

Introduction

Since Rundle and Fitzwater (*1*) obtained negative results when they tested $Nd_2(SO_4)_3 \cdot 8H_2O$ for pyroelectric properties, they assumed that the rare-earth sulfate octahydrates, which were known to be isomorphous (*2*), were centrosymmetric crystals. Therefore, they chose the centrosymmetric space group, $C_{2h}^6 - C2/c$ in their subsequent structure determination. Piezoelectric experiments conducted in this laboratory on the rare-earth sulfate octahydrates gave positive results indicating the crystals are definitely noncentrosymmetric. Because the structure derived by Rundle and Fitzwater was based on limited crystallographic data and placed in a centrosymmetric space group, it was decided that the structure should be redetermined.

Ivanov (*3*) reported the structure of $Gd_2(SO_4)_3 \cdot 8H_2O$ was under study but no report of the structure has appeared. Mascarenhas (*4*) recently reported the structure of $Ho_2(SO_4)_3 \cdot 8H_2O$ as belonging to the noncentrosymmetric space group, $C_s{}^4$–Cc, which agrees with the space group that was assigned to the octahydrates in this investigation.

The crystal structure of $La_2(SO_4)_3 \cdot 9H_2O$ appears to be poorly defined, as evidenced by the final $R_f = 0.24$ reported by Hunt, Rundle and Stosick (*5*). Based on crystallographic extinctions, either $P6_3/m$ or $P6_3$, a centro- or noncentrosymmetric space group could be chosen. Hunt et al. (*5*) chose $P6_3/m$ because of the crystal habit and the lack of pyroelectric effect. They attributed the inability to obtain an R factor lower than 0.43 for 129 reflections which contained no La contribution to poor intensity data. They also experienced difficulty in locating some of the oxygen atoms. Because of the uncertainties in the structure, its redetermination was warranted.

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Experimental

The results of chemical analyses of several of the octahydrates are given in Table I. The various octahydrates were tested for piezoelectric effect by deforming the crystal between copper plates using aluminium foil for electrodes. A Kintel Model 202B, microvolt meter was used to measure the conductance changes with pressure. Nd, Gd, Tb, Dy, and Ho sulfate octahydrates gave strong effects in the 30–100 mV range. The Eu salt, which was poorly crystallized, gave a small but measurable effect. It was observed that clear-green Pr crystals showed conductance, while Pr crystals which had remained open to the atmosphere were coated with a white powder and showed no conductivity when pressure was applied.

$Pr_2(SO_4)_3 \cdot 8H_2O$

A crystal of $Pr_2(SO_4)_3 \cdot 8H_2O$ was ground to a sphere, 0.0492 cm in diameter. The crystal is monoclinic with unit cell parameters $a = 13.675(3)$ Å, $b = 6.832(3)$ Å, $c = 18.426(3)$ Å, $\beta = 102.8(3)^\circ$, (from diffractometer measurements of 15 reflections, $2\theta > 12^\circ$) and $D_m = 2.89(3)$ g·cm^{-3} (measured by displacement in *n*-octane) and $D_c = 2.82$ g·cm^{-3}, $Z = 4$, space group $C_s^4 - Cc$ or $C_{2h}^6 - C2/c$. Because of the results of the piezoelectric tests, the noncentrosymmetric space group, C_s^4, was chosen. The linear absorption coefficient is 61.1 cm^{-1} for MoKα radiation. Intensity data were collected with a General Electric XRD-490 diffractometer for $2\theta = 0 - 50^\circ$ using MoKα radiation and balanced double filter (*Y–Zr*) peak height technique. Data from 1528 reflections, of which 1473 were independent, were collected in the octants hkl and $\bar{h}kl$. Two standard reflections were checked after each 20 data and were found to remain stable within 1% during the data collection. The intensity for a reflection was counted for 10 sec and the background was counted for 20 sec. Weights were assigned to the intensity data, using the formula $W = 1/\sigma^2$, where σ is the standard deviation of the net count.

$$\sigma I_{\text{net}} = \left[I_{\text{tot}} + t_c \left(\frac{B_1 + B_2}{t_B} \right) + 0.02 \left(I_{\text{tot}} - t_c \left(\frac{B_1 + B_2}{t_B} \right) \right) \right]^{1/2},$$

where I_{tot} is the total count, B is the background count, t_c is the counting time for the reflection, t_B is the counting time for the background and 0.02 is a fractional systematic error. Absorption and Lorentz-polarization corrections were made using the program DATALIB (*6*). The Pr atoms were located in a three-dimensional Patterson map prepared using the program FORDAP. For the least-squares calculations, the scattering curves and the anomalous dispersion corrections for praseodymium, lanthanum, oxygen, and sulfur were taken from the "International Tables for X-Ray Crystallography" (*7*). The Fourier map based on the least-squares refinement (XFLSAX program) with the Pr atoms only, revealed all other atoms except hydrogen ($R_f = 0.28$, where $R_f = \Sigma||F_0| - |F_c||/\Sigma|F_0|$).

TABLE I

RESULTS OF ANALYSES

Compound	Rare Earth		$(SO_4)^{2-}$		H_2O	
	Found (%)	Calculated (%)	Found (%)	Calculated (%)	Found (%)	Calculated (%)
$Ho_2(SO_4)_3 \cdot 8H_2O$	44.56	43.28	—[a]	37.70	19.53	18.91
$Sm_2(SO_4)_3 \cdot 8H_2O$	41.90	41.02	40.70	39.32	19.35	19.66
$Pr_2(SO_4)_3 \cdot 8H_2O$	39.07	39.46	40.28	40.36	19.80	20.18

[a] Analysis not performed.

TABLE II

POSITIONAL PARAMETERS AND THERMAL PARAMETERS[a] OF $Pr_2(SO_4)_3 \cdot 8H_2O$[b]

Atoms	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pr(1)[c]	0.28661	0.47359(15)	0.6074	0.00151(9)	0.00356(25)	0.00088(5)	0.00153(17)	0.00000(5)	0.00064(13)
Pr(2)	0.12504(6)	0.97513(15)	0.39301(5)	0.00078(8)	0.00561(27)	0.00084(5)	−0.00086(16)	−0.00009(5)	−0.00031(13)
S(1)	0.4580(5)	0.8292(4)	0.7512(4)	1.05(5)					
S(2)	0.1678(5)	1.0336(7)	0.5896(4)	0.72(10)					
S(3)	0.2390(5)	0.4711(8)	0.4121(4)	1.21(12)					
O(1)	0.1024(13)	1.0916(30)	0.5178(11)	2.72(35)					
O(2)	0.1209(13)	1.0142(21)	0.6508(10)	1.64(29)					
O(3)	0.2113(12)	0.8338(25)	0.5748(9)	2.23(31)					
O(4)	0.2506(10)	1.1795(23)	0.6027(8)	1.06(25)					
O(5)	0.3155(10)	0.4230(22)	0.4831(8)	0.73(23)					
O(6)	0.2977(13)	0.4511(21)	0.3547(9)	1.77(31)					
O(7)	0.1598(12)	0.3270(27)	0.3959(9)	2.05(31)					
O(8)	0.2006(11)	0.6546(22)	0.4181(9)	1.73(27)					
O(9)	0.4238(12)	0.0409(21)	0.8046(9)	1.02(31)					
O(10)	0.5329(12)	0.6945(25)	0.7839(9)	2.27(27)					
O(11)	0.3663(10)	0.7148(22)	0.7114(8)	1.54(25)					
O(12)	0.4926(15)	0.9376(31)	0.6916(11)	2.51(42)					
O(W1)	0.2082(11)	1.0226(19)	0.2945(8)	1.68(26)					
O(W2)	0.3087(10)	1.0038(19)	0.4584(8)	0.40(23)					
O(W3)	−0.0323(10)	1.1578(22)	0.3482(8)	2.13(27)					
O(W4)	0.4188(10)	0.7424(20)	0.5665(7)	0.76(25)					
O(W5)	−0.0045(13)	0.7316(27)	0.4381(9)	2.52(36)					
O(W6)	0.1876(11)	0.5206(20)	0.2043(9)	1.86(27)					
O(W7)	0.4416(9)	0.3268(20)	0.6358(7)	1.62(24)					
O(W8)	0.1088(13)	0.4687(23)	0.5389(10)	2.08(35)					

[a] The anisotropic thermal parameter is in the form of $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Anisotropic thermal parameters were applied to Pr and isotropic thermal parameters to the rest of the atoms.

[b] Estimated deviations are given in parentheses.

[c] The x and z parameter on Pr(1) was held constant in the least-squares refinement.

When all atoms were included, a structure factor calculation yielded $R_f = 0.14$. The full-matrix least-squares refinement with anisotropic thermal parameters for Pr and isotropic thermal parameters for the other atoms converged to a final $R_f = 0.047$. No parameter varied by more than $\Delta/\sigma = 0.37$ in the last cycle of refinement. On the final difference Fourier map the highest peaks were 3.49 $e/Å^3$. On checking the distances of these peaks to the atoms of the structure, all peaks between 1.10 and 3.49 $e/Å^3$ were less than 0.9 Å from the Pr, S, and O atoms. The large residuals are probably due to errors in the absorption corrections, weighting or scaling. Attempts to place the hydrogen atoms at locations of peaks and allow these positions to refine to positions with reasonable bond lengths and bond angles were unsuccessful. Final positional and thermal parameters for $Pr_2(SO_4)_3 \cdot 8H_2O$ are given in Table II. The observed and calculated structure factors are given in Table III.[1]

$La_2(SO_4)_3 \cdot 9H_2O$

La metal was dissolved in dilute sulfuric acid and upon evaporation $La_2(SO_4)_3 \cdot 9H_2O$ crystals were formed. The data crystal had dimensions of 0.06 × 0.06 × 0.071 cm. The crystal is hexagonal with unit cell parameters $a = 11.009(20)$Å, $c = 8.076(20)$ Å, (from diffractometer measurements of 14 reflections, $2\theta > 10°$) $Z = 2$, $D_c = 2.84$ g·cm^{-3} and $D_m = 2.82$ $g \cdot cm^{-3}$ (7). From extinction data the space group was determined as $C_6{}^6 - P_3{}^6$ or $C_{6h}^2 - P6_3/m$.

Intensity data were collected using a General Electric XRD-490 Automated Diffractometer for $2\theta = 0$–$50°$ using MoKα radiation and a θ–2θ step-scan technique. The scan width was 2° with steps of 0.1°. Each step was counted for 4 sec and the background on

TABLE IV

Positional and Thermal Parameters of $La_2(SO_4)_3 \cdot 9H_2O$[a]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La(1) (2b)	0	0	0	0.0055(2)	0.0055(2)	0.0013(2)	0.0055(2)	0	0
La(2 (2d)	0.3333	0.6667	0.75	0.0042(2)	0.0042(2)	0.0034(2)	0.0042(2)	0	0
S(6h)	0.2611(3)	0.0511(4)	0.25	0.0022(4)	0.0036(4)	0.0039(5)	0.0013(3)	0	0
O(1) (6h)	0.1671(1)	0.1125(1)	0.25	0.0042(11)	0.0030(11)	0.0064(14)	0.0027(9)	0	0
O(2) (6h)	0.4078(11)	0.1605(11)	0.25	0.0039(12)	0.0061(14)	0.0102(19)	−0.0008(11)	0	0
O(3) (12i)	0.2254(7)	0.9669(7)	0.0993(8)	0.0057(8)	0.0060(9)	0.0038(10)	0.0036(7)	−0.0004(8)	−0.0026(8)
O(W1) (6h)	0.3354(12)	0.4354(12)	0.25	0.0076(14)	0.0065(14)	0.0116(20)	0.0027(12)		
O(W2) (12i)	0.3816(8)	0.8441(8)	0.9799(9)	0.0069(9)	0.0080(10)	0.0080(12)	0.0043(8)	−0.0025(9)	−0.0044(9)

[a] Estimated standard deviations are given in parentheses.

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[1] Supplementary material (Tables III and V) has been deposited as Document No. NAPS 02883 with the National Auxiliary Publications Service, c/o Microfiche Publications, 440 Park Avenue South, New York, New York 10006. A copy may be secured by citing the document number and by remitting $5.00 for photocopy or $1.50 for microfiche. Advance payment is required. Make check or money order payable to Microfiche Publications.

each end of the scan was counted for 8 sec. Two standard reflections were checked after each 20 data and were found to be stable within 5% throughout the data collection. Weights were assigned to the intensity data using the same formula as described on the $Pr_2(SO_4)_3 \cdot 8H_2O$ structure except in this case the t_c represents the time scanning the reflection. Absorption ($\mu = 55.13$ cm^{-1}) and Lorentz-polarization corrections were made using the DATALIB program. In the refinement 624 independent reflections were used. The proposed locations for the La and SO_4 ions in the centrosymmetric space group, $P6_3/m$ reported by Hunt et al. were used in a least-squares calculation which yielded an initial $R_f = 0.15$. The subsequent Fourier map gave approximately the same locations given by Hunt et al. for the water molecules. A full-matrix least-squares refinement (isotropic thermal parameters) containing all oxygens of the water molecules yielded $R_f =$

TABLE VI

INTERATOMIC DISTANCES AND BOND ANGLES IN $Pr_2(SO_4)_3 \cdot 8H_2O$[a]

Pr(1)–Pr(2)	5.100(9) Å	–O(8)	2.36(2)	–O(10)	3.01(2)
–O(3)	2.36(2)	–O(7)	2.46(2)	–O(8)	3.01(2)
–O(11)	2.36(2)	O(6)–O(7)	2.34(2)	–O(6)	3.06(2)
–O(4)	2.42(2)	–O(8)	2.40(2)	O(W6)–O(12)	2.68(2)
–O(5)	2.51(1)	O(7)–O(8)	2.32(2)	–O(11)	2.76(2)
–O(W6)	2.47(2)	(O9)–O(11)	2.40(2)	–O(6)	2.85(2)
–O(W7)	2.48(1)	–O(10)	2.43(2)	–O(W8)	3.02(2)
–O(W8)	2.51(2)	–O(12)	2.47(2)	O(W7)–O(2)	2.73(2)
–O(W4)	2.57(1)	O(10)–O(12)	2.35(3)	–O(4)	2.74(2)
Pr(2)–O(10)	2.42(2)	–O(11)	2.38(2)	–O(12)	2.88(2)
–O(8)	2.42(1)	O(11)–O(12)	2.39(2)	–O(5)	3.03(2)
–O(7)	2.45(2)	O(W1)–O(2)	2.66(2)	O(W8)–O(1)	2.60(3)
–O(1)	2.52(2)	–O(10)	2.79(2)	–O(4)	2.84(2)
–O(W1)	2.37(1)	–O(9)	2.92(2)	–O(3)	2.87(2)
–O(W3)	2.47(1)	–O(7)	2.97(2)	–O(W5)	2.96(2)
–O(W2)	2.54(1)	–O(W2)	3.03(2)	–O(W6)	3.02(2)
–O(W5)	2.54(2)	O(W2)–O(8)	2.82(2)	–O(7)	3.03(2)
S(1)–O(10)	1.41(2)	–O(W4)	2.85(2)	–O(8)	3.06(2)
–O(9)	1.48(2)	–O(5)	2.90(2)	O(10)–S(1)–O(9)	114.5(10)°
–O(12)	1.49(2)	–O(3)	3.00(2)	O(10)–S(1)–O(12)	108.7(11)
–O(11)	1.52(1)	–O(W1)	3.03(2)	O(10)–S(1)–O(11)	108.3(7)
S(2)–O(2)	1.42(2)	–O(7)	3.05(2)	O(9)–S(1)–O(12)	113.2(8)
–O(1)	1.48(2)	O(W3)–O(6)	2.74(2)	O(9)–S(1)–O(11)	106.4(9)
–O(4)	1.49(2)	–O(9)	2.76(2)	O(12)–S(1)–O(11)	105.3(10)
–O(3)	1.54(2)	–O(7)	2.83(2)	O(2)–S(2)–O(1)	116.4(11)
S(3)–0(8)	1.37(2)	–O(10)	2.91(2)	O(2)–S(2)–O(4)	113.3(10)
–O(7)	1.45(2)	O(W4)–O(12)	2.66(2)	O(2)–S(2)–O(3)	108.5(9)
–O(6)	1.47(2)	–O(W2)	2.85(2)	O(1)–S(2)–O(4)	104.7(10)
–O(5)	1.52(2)	–O(5)	2.86(2)	O(1)–S(2)–0(3)	105.1(11)
O(1)–O(4)	2.35(2)	–O(11)	2.92(2)	O(4)–S(2)–O(3)	108.2(9)
–O(3)	2.39(2)	–O(3)	2.94(2)	O(8)–S(3)–O(7)	110.8(10)
–O(2)	2.46(2)	–O(1)	3.03(2)	O(8)–S(3)–O(8)	114.9(9)
O(2)–O(7)	2.40(2)	O(W5)–O(1)	2.87(2)	O(8)–S(3)–O(5)	109.4(9)
–O(4	2.43(2)	–O(9)	2.89(2)	O(7)–S(3)–O(6)	107.0(10)
O(3)–O(4)	2.45(2)	–O(5)	2.96(2)	O(7)–S(3)–O(5)	111.9(10)
O(5)–O(6)	2.33(2)	–O(W8)	2.96(2)	O(6)–S(3)–O(5)	102.6(10)

[a] Estimated standard deviations are given in parentheses.

0.074. The least-squares refinement using anisotropic thermal parameters for the La atoms led to $R_f = 0.067$. The final least-squares refinement with anisotropic thermal parameters on all atoms converged to $R_f = 0.063$. No positional parameter varied by more than 0.002 Å in the last cycle of refinement. The final difference Fourier map had peaks with a maximum height of 1.37 $e/\text{Å}^3$. Attempts to locate the hydrogen atoms were unsuccessful. Final positional and thermal parameters for $La_2(SO_4)_3 \cdot 9H_2O$ are given in Table IV. The observed and calculated structure factors are listed in Table V.[1]

Description and Discussion of Structures

$Pr_2(SO_4)_3 \cdot 8H_2O$

Projection of the structure of $Pr_2(SO_4)_3 \cdot 8H_2O$ onto (010) shows the rare-earth and sulfate positions are at the approximate locations given by Fitzwalter and Rundle, but the prior water locations were different due to the requirements of the assumed centro-

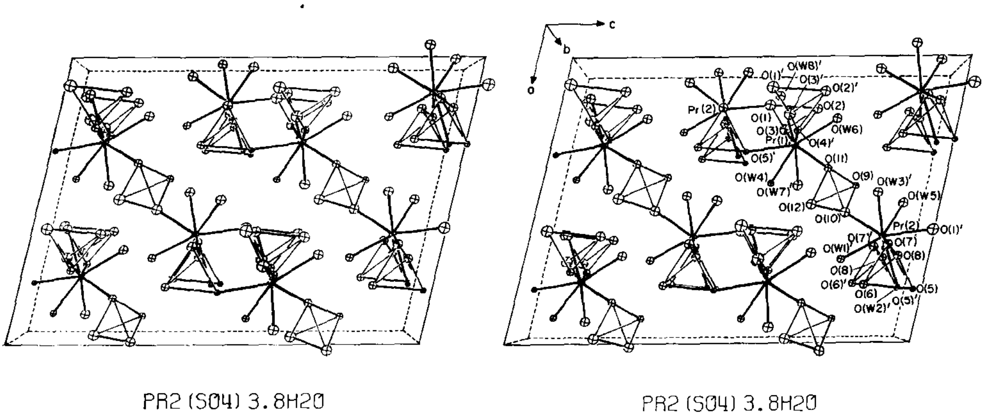

FIG. 1. Stereo projection of $Pr_2(SO_4)_3 \cdot 8H_2O$ illustrating the bonding around the Pr atoms. The sulfur atom is left out for clarity. One of the sulfate groups is in an adjoining cell.

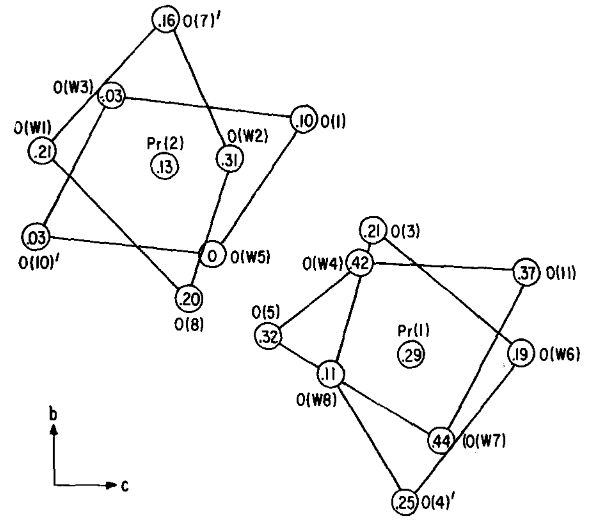

FIG. 2. Projection on (100) of the Archimedian antiprisms formed by the eight atoms bonded to the Pr atoms. The x coordinates of all atoms are shown in the circles.

symmetric space group. Bond distance calculations indicate 8 coordination for Pr, instead of 9 as reported by Fitzwater and Rundle (see Table VI). Using the centrosymmetric space group, the data refined only to $R_f = 0.18$. Therefore, one must conclude that the noncentrosymmetric space group is correct.

Each Pr is bonded to four sulfate groups and four water molecules as shown in Fig. 1. Note that one of the sulfate groups belongs to an adjoining unit cell. Figure 2 illustrates the extreme distortion of the Archimedian antiprism formed by the 8 atoms bonded to Pr. One oxygen atom from each of four sulfate groups is bonded to Pr. Two sulfate groups are bonded to three Pr's and the third sulfate group is bonded to two rare-earth atoms. The Pr–O(SO_4) bond lengths range from 2.36(2) to 2.52(2) Å and the Pr–O(H_2O) bond lengths range from 2.37(1) to 2.57(1) Å (see Table VI). The next nearest neighbor to the Pr atoms are oxygen atoms in a fifth sulfate group at 3.37 and 3.57 Å. Mascarenhas (*4*) reported interatomic distances Ho–O ranging from 2.26(5)–2.46(5) Å in $Ho_2(SO_4)_3 \cdot 8H_2O$. The sulfate group is $Pr_2(SO_4)_3 \cdot 8H_2O$ has S–O bonds of 1.37(2)–1.54(2) Å, 0–0 distances of 2.32(2)–2.37(2) Å, and 0–S–O angles between 102.6(10)–116.4(11) with an average angle of 109°. Marcarenhas found S–O distances of 1.42–1.47 Å, and O–S–O angles between 109 and 113° in $Ho_2(SO_4)_3 \cdot 8H_2O$. The sulfate tetrahedron in the Pr salt is significantly more distorted than that observed for the Ho salt. The S(3)–O(8) bond length of 1.37(2) Å is shorter than the normal S–O distance but well within 3σ of the range of 1.44–1.53 (±4) Å given in the "International

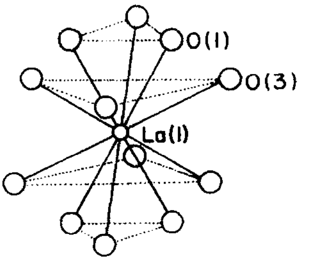

FIG. 3. Coordination around La(1) in $La_2(SO_4)_3 \cdot 9H_2O$.

TABLE VII

INTERATOMIC DISTANCES AND BOND ANGLES IN $La_2(SO_4)_3 \cdot 9H_2O$[a]

Atoms	Number of bonds	Interatomic distances (Å)
La(1)–La(1)		4.038(10)
La(1)–O(1)	6	2.591(7)
La(1)–O(3)	6	2.800(8)
La(2)–O(2)	3	2.513(11)
La(2)–O(W2)	6	2.551(8)
S–O(1)	1	1.492(9)
S–O(2)	1	1.454(11)
S–O(3)	2	1.460(7)
O(1)–O(2)	1	2.430(15)
O(1)–O(3)	2	2.344(10)
O(2)–O(3)	2	2.403(11)
O(*W*1)–O(W2)	2	2.820(11)
–O(1)	1	3.080(15)
–O(3)	2	3.141(14)
O(*W*2)–O(2)	1	2.818(12)
–O(3)	1	2.820(11)
–O(2)	1	2.835(10)
O(1)–S–O(2)	1	111.1(6)
O(2)–S–O(3)	1	111.1(4)
O(1)–S–O(3)	1	105.1(4)
O(3)–S–O(3)	1	112.9(6)
O(1)–La(1)–O(1)	1	180.0(0)
O(1)–La(1)–O(1)	2	65.8(3)
O(1)–La(1)–O(1)	2	114.2(3)
O(3)–La(1)–O(3)	1	180.0(0)
O(3)–La(1)–O(3)	2	112.1(1)
O(3)–La(1)–O(3)	2	67.9(2)
O(1)–La(1)–O(3)	1	51.4(2)
O(1)–La(1)–O(3)	1	128.6(2)
O(1)–La(1)–O(3)	1	65.8(2)
O(1)–La(1)–O(3)	1	114.2(2)
O(1)–La(1)–O(3)	1	111.4(2)
O(1)–La(1)–O(3)	1	68.6(2)
O(2)–La(2)–O(2)	2	120.0(1)
O(*W*2)–La(2)–O(*W*2)	1	93.4(4)
O(*W*2)–La(2)–O(*W*2)	2	72.9(3)
O(*W*2)–La(2)–O(*W*2)	2	139.2(2)
O(2)–La(2)–O(*W*2)	2	67.6(3)
O(2)–La(2)–O(*W*2)	2	72.4(3)
O(2)–La(2)–O(*W*2)	2	133.2(2)

[a] Estimated standard deviations are given in parentheses.

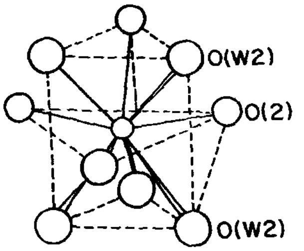

FIG. 4. Coordination around La(2). The water-oxygens form a trigonal prism with sulfate–oxygens on the faces.

Tables of Crystallography" for the SO_4^{2-} ion (*9*). The S–O–Pr distances range from 3.88–4.03 Å except for two cases where they are considerably shorter. The S(3)–O(8)–Pr(2) distance is 3.79 Å and the S(1)–O(10)–Pr(2) distance is 3.82 Å. In both cases the Pr–O distance is 2.42 Å, very near the average Pr–O distance of 2.43 Å. Although attempts to locate the hydrogen atoms were unsuccessful, the bond lengths, 2.60(3)–3.06(2) Å between the oxygen atoms in the sulfate groups and water molecules are within the range of hydrogen bonding reported from neutron diffraction studies (*10*).

The Pr atoms are bonded to sulfate groups so there is a chain extending diagonally through the cell in the *ac* projection and also in the *b* direction as shown in Fig. 1. There is also a suggestion of strong hydrogen bonding between O(1)–O(*W*8), O(2)–O(*W*1), and O(12)–O(*W*4), where the O–O distances are 2.60(3), 2.66(2) and 2.66(2) Å, respectively. Numerous weaker hydrogen bonds of O–O = 2.7–3.1 Å are also apparent. All interatomic distances and bond angles for $Pr_2(SO_4)_3 \cdot 8H_2O$ are listed in Table VI.

$La_2(SO_4)_3 \cdot 9H_2O$

The La ion, situated at the corner of the unit cell, is bonded to 12 oxygen atoms in the manner shown in Fig. 3. There are three sulfate groups below and three above each La(1) in the direction of the *b*-axis. The La(1) is bonded to O(1) and O(3) of each sulfate group and the La(1)–O bond lengths are 2.591(7) and 2.800(8) Å, respectively (see Table VIII). Hunt et al. had repored 2.60 and 2.74 Å for the La–O bond distances. The La(2) ion is bonded to three oxygens from three sulfate groups and six water–oxygens in the form of a trigonal prism (see Fig. 4). The

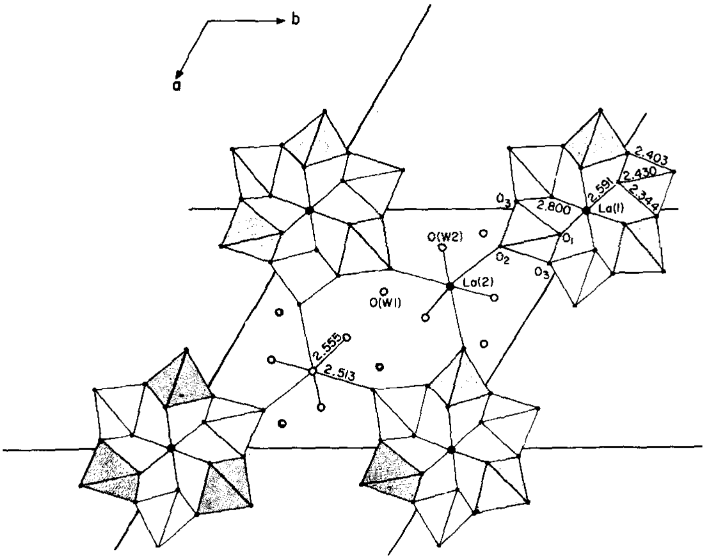

FIG. 5. Projection of $La_2(SO_4)_3 \cdot 9H_2O$ on (001). The center of the shaded sulfate tetrahedrons and the shaded La(2) and O(*W*2) are at $z = \frac{3}{4}$. The open sulfate tetrahedrons and open La(2) are at $z = \frac{1}{4}$. The La(1) is at $z = 0$ and O(*W*2) is at $z = 0$ and $z = \frac{1}{2}$.

La(2)–O(2) bond distance is 2.513(11) Å while the La(2)–O(W2) bond length is 2.555 (8) Å. These distances are much shorter than the 2.74 Å reported by Hunt *et al.* but within the range of 2.42–2.89 Å found in La_2O_3 (*11*). The other water-oxygen, O(*W*1), apparently has a space-filling role in the structure. Its nearest neighbor is the other water-oxygen, O(*W*2), at a O–O distance of 2.820(11) Å and the next nearest neighbor is O(1) at 3.080(15) Å. The water-oxygen, O(*W*2), which is bonded to the La(2) may be involved in hydrogen bonding with the sulfate oxygens since the oxygen separations range from 2.818(12)–2.835(10) Å. Attempts to locate the hydrogens were unsuccessful. The hydrogen bonding in the $La_2(SO_4)_3 \cdot 9H_2O$ is obviously weaker than that in $Pr_2(SO_4)_3 \cdot 8H_2O$, where some $O(SO_4)$–$O(H_2O)$ distances are as short as 2.630 Å. The bond lengths and angles are given in Table VII. Figure 5 is (001) projection of $La_2(SO_4)_3 \cdot 9H_2O$.

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Note added in proof. In private communication with Y. Mascarenhas I am informed that there was a printing error in Ref. 4: She assumed the space group to be centrosymmetric, as did other workers (*12–14*). Her crystals are in the process of being tested for noncentrosymmetry by the second harmonic analyzer technique. When I became aware of later studies (*4*, *12–14*) on isomorphorous compounds, I checked my data using their model. The resulting Pr–O and S–O bond lengths and angles are in a narrower range with smaller errors, but the *R* factor is slightly higher and the residual e.s.d.'s are approximately the same. The basic structure is the same in each model except the diagonal chain formed by Pr and the sulfate ion is displaced approximately one-half the unit cell in the *b* direction. Only reliable, independent physical tests for noncentrosymmetry can determine which is the preferred structure.

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