Refinement of the Alum Structures. I. X-Ray and Neutron Diffraction Study of CsAl(SO₄)₂.12H₂O, a β Alum*

BY DON T. CROMER

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A. and Puerto Rico Nuclear Center, Mayaguez, Puerto Rico

M. I. Kay

Puerto Rico Nuclear Center, Mayaguez, Puerto Rico

AND ALLEN C. LARSON

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

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The structure of CsAl(SO₄)₂. 12H₂O, a β alum, has been refined from three-dimensional X-ray diffraction data and neutron diffraction data from the *hk*0 zone. The maximum shift in atom positions from those given by Lipson (1935) is only 0.04 Å. Criteria for classifying alums as α , β or γ types are discussed.

Introduction

The alums are a large class of double salts having the general formula $A^+B^{3+}(RO_4)_2$. $12H_2O$ where A can be NH₄, CH₃NH₃, Na, K, Rb, Cs; B can be Al, Ga, Cr, Fe, V; and R can be S, Se or Te. BeF₄²⁻ alums are also known. These compounds are cubic, space group *Pa3*, although this symmetry can only be achieved statistically with the ammonium and substituted ammonium alums. The alums were all thought to be isomorphous until the X-ray work of Lipson (1935) showed that there are three different types which he named α , β and γ , in the order of their discovery.

The type of alum formed depends on the size of the monovalent cation. If the cation is small the γ alum forms. The only known representative of this class is NaAl(SO₄)₂. 12H₂O. The β alum forms if the cation is large and the α alum, which is by far the most common type, occurs if the cation is of intermediate size. In all the alums there are two crystallographically different water molecules, each associated exclusively with either the monovalent or trivalent cation. The trivalent cation is always surrounded by six water molecules in a nearly regular octahedron but the orientation of the octahedron with respect to the cell axes is different in each of the three types. The monovalent cations in the α and γ alums also have six water molecules. In γ alum these water molecules form a nearly regular octahedron. In α alum the octahedron is distorted by compression along the threefold axis.

The large cation in β alums can accommodate 12 oxygen neighbors. To attain this large coordination number the water octahedron is compressed along the

threefold axis and stretched out normal to this axis until it is nearly planar. The two ends of the resulting trigonal antiprism are separated by only about 0.06 Å. The sulfate groups at each end of this antiprism are then moved along the threefold axis toward the central cation until six sulfate oxygen atoms are about the same distance from the cation as are the water molecules. A slightly distorted cubic close packed array of oxygen atoms thus surround the cation.

In the γ structure six water molecules approach the small sodium cation much more closely than in the α structure. This motion cannot take place unless the hydrogen bonding system changes. The most striking result is that the sulfate groups become oppositely oriented along the threefold axis.

Discussions of the relations among the three structures have been given by Lipson (1935) and by Jona & Shirane (1962). None of the alums has been investigated by modern counting techniques although Okaya, Ahmed, Pepinsky & Vand (1957) have studied methylammonium aluminum sulfate dodecahydrate (MASD) by photographic methods and refined the structure by least squares. Okaya et al. (1957) do not classify MASD in a particular structure type because 'the difference between α and β alum types is not adequately defined structurally'. On the other hand we believe that the three structure types may be clearly distinguished and that MASD is a member of the β alums. The characteristic that distinguishes the y alums from the α and β alums is the orientation of the sulfate group. In the γ alums this group is oriented opposite to its orientation in the α and β alums. The β alums have twelvefold and the α alums have sixfold coordination of oxygen about the central monovalent cation. Okaya et al. (1957) probably overlooked this difference in coordination because the distances which they state are from the

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center of gravity of the $CH_3NH_3^+$ ion are actually from the nitrogen or carbon atoms of the disordered ion.

We have investigated several of the alums by both X-ray and neutron diffraction methods. The present paper concerns the structural refinement of $CsAl(SO_4)_2$. $12H_2O$, an example of the β alum type.

Experimental

Crystals for the X-ray study were grown from a water solution. Well formed octahedra, sometimes with small {100} and {110} forms developed, were readily obtained, and spheres were ground in a Bond sphere grinder. A sphere 0.16 mm in diameter was used in obtaining the intensity data. The lattice constant was measured with a carefully aligned single-crystal orienter on a General Electric XRD-5 X-ray diffraction unit and found to be 12.352 ± 0.003 Å (Mo $K\alpha_1 = 0.70926$ Å) in reasonable agreement with 12.358 ± 0.002 Å reported by Lipson & Beevers (1935). Mo $K\alpha$ radiation and Zr-Y balanced filters were used in measuring the intensities within the range $2\theta \le 50^\circ$ by both the fixed crystal, fixed counter method and the 2θ scan method. Onefourth of the hemisphere was measured by the former technique and one-sixth by the latter. Thus, equivalent reflections were measured three times by the fixed crystal method and twice by the 2θ scan method. No absorption corrections were necessary ($\mu R = 0.19$). The internal consistency of the data was estimated by forming the indices $R_F = \sum |F_i - (\overline{F^2})^{\frac{1}{2}}| / \sum (\overline{F^2})^{\frac{1}{2}}$ and $R_{F^2} =$ $\Sigma |F_i^2 - \overline{F_i^2}| / \Sigma \overline{F_i^2}$ where the summations were taken over all reflections observed more than once. These values and the number of observations are given in Table 1. The internal consistency is better with the 2θ scan data but this is partly the consequence of comparing only two equivalent reflections rather than three. If the assumptions are made that the measurements are normally distributed, and that for the case of three equivalent measurements the mean is equal to the median, then R_F for two measurements should be about 1.5 times that for three measurements (Dixon & Massey, 1957).

Table 1. Summary of observed X-ray data

Nu equiv	mber of non- alent reflections measured	Number observed	R_F	R_{F^2}
Fixed crystal	557	362	0.0199	0.0242
29 Scan	557	320	0.0097	0.0111

Reflections were considered observed if $(I-Back-ground) \ge 3.0 \times (I+Background)^{\frac{1}{2}}$. Because the contrast between the intensity and the background is greater for the fixed crystal method more reflections are observed by this technique.

For neutron diffraction studies larger crystals are necessary. Fine wires were suspended in a supersaturated solution of cesium alum and numerous small crystals formed on these wires. Most of the crystals were scraped from the wires and the remainder were suspended in a saturated solution which was then allowed to evaporate slowly. An octahedron, 4 mm on an edge, was selected for study. The fine wire remaining inside the crystal was assumed to have a negligible effect on the neutron scattering. The crystal was briefly immersed in liquid nitrogen to increase its mosaic nature and thus reduce the effects of extinction. The neutron diffraction intensities of the hk0 zone were measured with the single-crystal spectrometer at the Puerto Rico Nuclear Center. A wavelength of 1.06 Å was used, and non-equivalent reflections within the range $2\theta \le 90^\circ$ were measured by step scanning. Of these, 64 were observed according to the criterion $(I-\text{Background}) \geq$ $2.0 \times (I + \text{Background})^{\frac{1}{2}}$. Because of the large incoherent scattering of hydrogen, absorption corrections were applied. The linear absorption coefficient for cesium alum is 4.31 cm⁻¹. Calculated transmission factors were between 0.292 and 0.353.

Refinement of the structure with X-ray data

The atomic positions given by Lipson (1935) were used as starting values for a full-matrix least-squares refinement of all non-hydrogen parameters. Anisotropic thermal parameters were used in the form

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\right].$$

The scattering factors of Cromer & Waber (1965) were used for cesium, aluminum and sulfur, and that given in *International Tables for X-ray Crystallography* (1962) was used for oxygen. Since the anomalous dispersion for cesium is small, no correction was made. The quantity minimized was $\Sigma w(F_o - F_c^*)^2$. Two weighting systems were used, $w = w_E$ and $w = w_E/(F_o + 0.02F_o^2)$ where w_E is the weight based on counting statistics as given by Evans (1961).

$$F_{c}^{*} = \frac{KF_{c}}{\left\{1 + g\left[\frac{2(1 + \cos^{4}2\theta)}{(1 + \cos^{2}2\theta)^{2}}\right] LpF_{c}^{2}\right\}^{4}}$$

where K is a scale factor, g is an extinction parameter (Zachariasen, 1963), Lp is the Lorentz and polarization factor, and F_c is the ordinary calculated structure factor. For unobserved reflections w=0. At the end of the refinements $\Delta \xi_i / \sigma(\xi_i) < 10^{-3}$ for all parameters ξ .

Both sets of data were refined with both weighting systems and nearly identical results were obtained. However, when the modified weights, *i.e.* $w = w_E/(F_o + 0.02F_o^2)$, were used the standard deviations were about 40% smaller, the S-O bond lengths were more nearly the same and the parameters obtained from the two different data sets were in closer agreement. With either data set the maximum parameter difference as a function of weighting system was about one standard deviation but for most parameters was considerably less.

The values of the residuals, R, with unobserved reflections omitted are given in Table 2 for both the fixed crystal and 2θ scan methods. To our knowledge, no detailed comparison of these two experimental techniques has appeared in the literature, at least not for a crystal as complex as a β alum. Cromer, Larson & Roof (1960) compared results for CeCu₆ obtained by the Evans (1953) method, which is a scan by moving the Weissenberg dial angle, ω , and by the fixed-crystal,

Table 2. R values for different sets of data

	$R = \Sigma \Delta F / \Sigma F_o $	$R_w = \Sigma w \left \Delta F \right / \Sigma w \left F_o \right $
Fixed crystal		
$w = w_E$	0.0394	0.0380
$w = w_E/(F_o + 0.02F_o^2)$) 0.0354	0.0528
2θ Scan		
$w = w_E$	0.0418	0.0356
$w = w_E/(F_o + 0.02F_o^2)$) 0.0375	0.0201
Neutron data		
$w = w_E/(F_o + 0.02F_o^2)$) 0.0744	0.0590

fixed-counter method. For various reasons, however, the CeCu₆ data did not provide a good comparison of the fixed crystal and scan techniques. Consequently it is of interest to report here in detail the results obtained by using both of these experimental techniques.

Table 3 gives the final least-squares parameters for the two sets of data. In nearly all cases the parameter differences are smaller than a standard deviation. The thermal parameters obtained from the fixed crystal data, however, are systematically slightly larger, probably because at higher angles a small portion of the intensity is lost because of $\alpha_1-\alpha_2$ separation. This effect is not nearly as pronounced with the alum as it was with CeCu₆ because with the alum the data were limited to 50° 2 θ whereas with CeCu₆ the data extended to 90° 2 θ . It is clear that the fixed-crystal method gives

Table 3. Least-squares parameters for CsAl(SO₄)₂. 12H₂O from X-ray diffraction data

The upper numbers are from the fixed crystal data and the lower numbers from the 2θ scan data. $w = w_E/(F_o + 0.02F_o^2)$ in both cases

Atom Cs	x 0·5 0·5	y 0·5 0·5	2 0·5 0·5	$B_{11} \times 10^5$ 428 ± 7 404 ± 7	$B_{22} imes 10^5 \ B_{11} \ B_{11}$	$B_{33} imes 10^5$ B_{11} B_{11}	$B_{12} imes 10^5$ - 88 ± 10 - 84 ± 15	$B_{13} \times 10^5$ B_{12} B_{12}	$B_{23} imes 10^5$ B_{12} B_{12}
Al	0·0 0·0	0·0 0·0	0·0 0·0	$218 \pm 15 \\ 186 \pm 15$	$B_{11} \\ B_{11}$	$B_{11} \\ B_{11}$	$\begin{array}{c} 54\pm36\\ 18\pm50 \end{array}$	$B_{12} \\ B_{12}$	$B_{12} \\ B_{12}$
S	0.32867 ± 15 0.32865 ± 19	x x	x x	217 ± 9 211 ± 11	$B_{11} \\ B_{11}$	$B_{11} \\ B_{11}$	$59 \pm 22 \\ 60 \pm 31$	$B_{12} \\ B_{12}$	$B_{12} \\ B_{12}$
Os(1)	0.25955 ± 40 0.25935 ± 48	x x	x x	$\begin{array}{r} 402\pm34\\ 384\pm38\end{array}$	$B_{11} \\ B_{11}$	$B_{11} \\ B_{11}$	$-220 \pm 66 \\ -241 \pm 87$	$B_{12} \\ B_{12}$	$B_{12} \\ B_{12}$
Os(2)	0.27893 ± 42 0.27869 ± 53	0.34108 ± 42 0.34096 ± 55	0.43637 ± 40 0.43681 ± 49	$\begin{array}{r} 486 \pm 43 \\ 484 \pm 53 \end{array}$	$340 \pm 41 \\ 338 \pm 54$	250 ± 38 212 ± 47	$\begin{array}{c} 143 \pm 70 \\ 150 \pm 93 \end{array}$	$313 \pm 67 \\ 331 \pm 81$	$\begin{array}{c}91\pm65\\133\pm82\end{array}$
Ow(1)	-0.15928 ± 43 -0.15917 ± 57	0.05065 ± 43 0.05129 ± 54	0.28465 ± 40 0.28488 ± 52	$\begin{array}{c} 323\pm40\\ 285\pm53 \end{array}$	$\begin{array}{r} 366\pm40\\ 358\pm50 \end{array}$	$401 \pm 39 \\ 390 \pm 50$	$10 \pm 70 \\ -6 \pm 89$	$116 \pm 69 \\ 162 \pm 90$	$\begin{array}{r} 25\pm70\\-5\pm86\end{array}$
$O_w(2)$	0.15236 ± 41 0.15261 ± 44	-0.00199 ± 37 -0.00209 ± 50	0.00001 ± 40 - 0.00138 ± 56	$\begin{array}{c} 203\pm34\\ 187\pm38 \end{array}$	$\begin{array}{r} 329\pm38\\ 308\pm42 \end{array}$	$399 \pm 42 \\ 385 \pm 45$	$40 \pm 69 \\ 21 \pm 101$	$\begin{array}{c}103\pm63\\50\pm86\end{array}$	$-3\pm 63 \\ 54\pm 91$

g $1.74 \pm 31 \times 10^{-7}$ $1.58 \pm 32 \times 10^{-7}$



Fig.1. Neutron diffraction difference Fourier synthesis showing hydrogen atoms only. Contours are at equal arbitrary units. Heavy lines are positive contours, light lines negative and the zero contour is dotted.

Table 4. Observed and calculated structure factors for CsAl(SO₄)₂. 12H₂O

The column headings are k, $10|F_o|/K$, and $10F_c^*/K$ (see text). If $|F_o|$ is negative the minus sign means 'less than'.

H= 1 L	- 1	H= 6 L= 3	H= 8 L= 3	H. 9 L. 7	H# 10 L* 9	H= 12 L= 3
1 910-	1034	1 -86 7	4 -101 -9	5 148 -126	5 -130 10	4 -125 106
H= 2 L	• •	3 -99 48	6 -108 -60	7 -137 -131	H= 11 L= 1	6 -124 11
0 1478	1518	4 102 89 5 -95 9	7 -107 8	8 -127 35	1 420 -424	7 -131 41
1 1294	1300	6 -103 86			2 212 221	H= 12 L= 4
	2340	H= 6 L= 4			4 158 -114	0 671 887
H= 2 L	- 1	0 1924 1869	0 1748 1790 1 -101 -19	0 167 -173 1 232 242	5 415 -426 6 -124 95	1 132 -80
1 445	-491 -871	1 -92 -8	2 541 549	2 -122 88	7 335 -321	3 -121 -45
		3 198 -214	4 1121 1122	4 -120 -64	9 321 -325	5 144 -119
H= 2 L	• 2	5 -100 44	5 243 226 6 1C20 986	5 161 -136 6 -120 -6	H= 11 L= 2	6 405 404 7 -130 -74
2 1828	1872	6 1097 1105	7 -114 1	7 233 239	0 427 -455	H= 12 L= 5
H= 3 L	- 1	H= 6 L= 5			1 207 -199	
1 665	-688	1 152 142		No 10 1. 0	3 -118 99	2 337 -349
2 -74 3 2628-	2504	2 502 -494 3 306 -313	1 161 154	0 573 533	4 -115 6 5 -119 69	3 -125 -18
		4 528 524	3 341 -329	2 1143 1161	6 181 -158	5 -130 -51
	• •	6 -110 -102	5 307 293	4 545 521	6 -126 116	6 -135 -51
1 1155	601 1116	H= 6 L= 6	6 -112 103 7 -116 57	5 -143 154 6 1148 1194	9 -135 103	H= 12 L= 6
2 651	-555	4 1944 2007	8 -118 62	7 493 -514	H= 11 L= 3	0 1086 1100
	-10	0 1 104 2001	H= 8 L= 6	9 -126 111	1 470 -496	2 614 616
н. 3 С	- 3	H= 7 L= 1	0 696 680	10 551 560	2 323 -334 3 1066-1090	3 -127 -25
3 2290-	2145	1 165 -174	1 311 297	H= 10 L= 1	4 188 172	5 -141 -115
H= 4 L	• 0	3 1268-1242	3 -113 -111	1 256 231	6 -131 -181	H# 12 L= 7
0 2969	2767	5 209 -224	5 391 -410	3 420 -445	7 226 -198 8 131 -110	1 -125 -31
2 835	950	6 -98 -28 7 135 -125	6 931 963 7 229 221	4 -111 56 5 273 287	9 805 -828	2 161 172
3 494	-439	H. 7	8 975 981	6 -117 -16	H= 11 L= 4	4 251 -259
- 1/31			H= 8 L= 7	8 -122 24	0 315 332	H# 12 L= 8
H= 4 L	+ 1	0 728 711 1 258 232	1 161 -137	9 245 -226 10 -135 72	1 444 463 2 310 -324	0 629 636
1 168	-90	2 496 -488	2 309 -305	H= 10 · - 2	3 -113 -44	1 -135 -101
3 338	- 364	4 -97 -54	305 303		5 305 -319	
	eu -	6 361 348	6 146 -130	1 272 247	7 329 332	- 13 L= 1
H= 4 L	* 2	7 -107 -11	7 -123 -78 8 179 -179	2 697 652 3 161 127	8 162 -128	1 266 -253 2 167 -1AR
0 2549	2569	H= 7 L- 3	Ha A 14 4	4 744 750	H= 11 L= 5	3 214 -217
2 1761	1837	1 384 -391		6 696 683	1 545 -559	5 214 -206
3 372	341 506	2 595 579 3 1148-1156	8 632 631	7 260 250 8 485 479	2 263 275 3 363 -370	6 -128 -10
H= 4 I	• •	4 269 -258 5 831 -846	H= 9 L= 1	9 -138 -147	4 -116 32	H# 13 L# 2
	_	6 163 144	1 607 -613		6 181 183	0 170 167
2 476	435	/ 100 -1/2	3 928 -920	H- 10 L- 3	8 165 137	2 -131 -50
3 208	-236	H- 7 L- 4	4 -108 -53 5 436 -448	1 -119 3 2 173 124	H= 11 L= 6	3 -123 80
No. 4. I		0 737 -766	6 -106 80 7 670 -687	3 -111 97	0 -124 -92	5 -124 37
		2 362 411	8 -118 -5	5 -112 46	1 -122 72	0 240 302
• • • • •	1004	4 163 144	4 443 -476	7 -116 0	3 -122 16	H= 13 L= 3
H= 5 L	- 1	5 547 -516 6 481 -492	H= 9 L= 2	8 -116 -28 9 -125 79	4 -116 4 5 -120 -30	1 201 -204
1 1121-	1185	7 319 336	0 -152 -84	10 -126 -31	6 -128 -48	3 361 -378
3 487	-520	H= 7 L= 5	2 -107 64	H= 10 L= 4		5 307 -317
5 923	-937	1 805 -774	4 -107 -5	0 826 820	H= 11 [- 7	6 -137 92
H= 5 L	- 2	2 446 -433 3 719 -713	5 159 -139 6 -110 -51	1 216 219	1 386 -379	H= 13 L= 4
0 334		4 155 137	7 226 211	3 248 -265	3 303 -304	0 268 -236
1 592	-562	6 143 -136	9 139 -120	5 -124 -115	5 288 -291	2 -126 47
2 373	-335	7 275 -260	H= 9 L= 3	5 862 858 7 -120 -46	6 -129 -81	3 -127 -65
4 608	588	H= 7 L= 6	1 1461-1475	8 523 513	H= 11 L= 8	5 -130 70
		0 139 -130	2 -107 -90		0 332 -317	H= 13 L= 5
		2 -104 -13	4 321 315	N= 10 [- 3	2 -130 135	1 312 -304
2 731	-720	4 183 -197	6 -114 -8	2 140 125	4 -130 -15	2 208 -211 3 364 -362
3 1686-	1680	5 182 -207 6 -114 49	7 505 -485 8 -115 53	3 403 394 4 -121 -124	5 -128 80	4 -139 168
5 998-	1000	7 163 167	9 285 -284	5 245 -272	H= 11 L= 9	H= 13 L= 6
н- 5 с	.= 4	H= 7 L= 7	H= 9 L= 4	7 -120 -19	1 352 -355	0 -135 93
0 -89	-43	7 532 -553	0 147 133	8 198 196 9 200 179	2 -131 -106 3 550 -553	1 -131 -19
1 143	-139	H= 8 I= 0	1 627 -633	H= 10 I = 4	HH 12 1 H 0	3 - 131 - 1
3 -89	-21		3 -105 12			H= 14 L= 0
• 601 5 -99	-623	0 1140 1165 1 318 309	4 122 -95 5 569 581	0 774 779	0 1515 1567 1 -124 -77	0 684 722
H= 5 L	- 5	2 1870 1919 3 565 554	6 -122 124 7 408 -430	2 974 981 3 193 208	2 925 928 3 -125 -34	1 313 324 2 848 840
		4 1440 1393	8 -124 -107	4 710 706	4 833 841	3 -128 55
2 031		6 1090 1100	7-161 16	6 613 602	6 965 971	
H= 6 1	- 0	7 522 367 8 1403 1427	H	8 648 655	8 464 455	H- 14 L- 1
0 3150	3081		1 256 -230			1 -128 -49
1 -88	47	H= 8 L= 1	2 -105 37	H= 10 L= 7	H= 12 L= 1	2 187 -144
2 2931	2849	1 189 -170	4 171 -176	1 213 245	1 -124 4	s 200 154 4 -145 156
4 1277	1289	2 287 -283	5 423 -398	2 -117 35	2 316 292	H= 14 L= 3
6 2339	2363	4 268 270	7 487 -496	-118 -24	4 332 -336	
H= 6	L= 1	5 176 -180 6 -108 -12	8 -123 53 9 798 -803	5 321 334 6 -123 -4	5 -119 47 6 -133 118	0 927 964 1 199 -203
1 144	-130	7 -106 28	H. 9 I. 4	7 147 111	7 -131 -140	2 428 439
2 405	424	u 113 -210		Un 10	u 19 ··· -	- 10 -1
3 385 4 318	-349	~* 5 L* 2	1 -115 -113	- LU L= 8	n= 12 L= 2	N# 14 L#]
5 370	-373	0 1801 1789 1 176 -174	2 -118 -94 3 -114 -10	0 698 688 1 247 265	0 427 383 1 -120 41	1 -129 12
		2 1149 1157	-110 -12	2 672 657	2 845 856	3 -131
H# 6	.* 2	5 935 927	6 -123 -105	4 523 514	4 794 761	H= 14 L4 4
0 1528	1485	5 -107 -87 6 1401 1401	7 -118 -44 8 -117 15	5 150 -136 6 627 622	5 199 186 6 616 619	0 664 685
2 1191	1150	7 416 -426	9 -135 -109	7 -137 118	7 -136 -137	i -135 -0
4 1911	1880		H= 9 L= 7	H= 10 L= 9	U 132 700	
5 -96 6 1212	81 1164	H= 8 L= 3	1 418 -423	1 -124 64	H= 12 L= 3	
		1 -99 46 2 -99 *	2 156 148	2 -125 1 3 -131 81	1 -115 47 2 161 -151	
		3 - 101 - 33	4 -115 36	4 -126 -45	3 -119 -33	

data that are quite satisfactory and, unless accurate thermal parameters are of particular interest, we prefer this method. More reflections are observed and thus the standard deviations of atomic positions are smaller. Also, the fixed crystal method is much faster. It takes perhaps one-fifth the time required by the scan method, although if a fully automated system is used this time differential may be unimportant.

Table 4 gives the observed and calculated structure factors for the fixed crystal data. A similar table for the 2θ scan data can be obtained from the authors.

Refinement of the structure with neutron diffraction data

Structure factors were calculated by using the parameters obtained from the X-ray analysis but without any hydrogen contribution. The structure factors were initially scaled so that $\Sigma F_o = \Sigma F_c$ and a difference Fourier synthesis was calculated. Approximate hydrogen positions were obtained and a least-squares refinement minimizing $\sum w(F_o - KF_c)^2$ was calculated where w = $w_E/(F_o + 0.02F_o^2)$, the symbols having the same meanings as given above. Parameters in this refinement were isotropic temperature factors for each crystallographically different atom, the scale factor and coordinates of the hydrogen atoms. The sulfur and oxygen atoms were not allowed to move. Table 5 gives the final parameters, and Table 6 gives the observed and calculated structure factors. The R indices are in Table 2. Fig.1 is a difference Fourier synthesis showing hydrogen atoms only.

Table 5. Least-squares parameters for $CsAl(SO_4)_2$. 12H₂O from neutron diffraction data Equivalent isotropic thermal parameters from X-ray data are

in parenthesis.							
Atom	В	x	У	Z			
H(1) H(2) H(3) H(4) Cs Al S $O_s(1)$ $O_s(2)$ $O_w(1)$	$\begin{array}{c} 2\cdot8\pm0.7\\ 2\cdot2\pm0.5\\ 1\cdot6\pm0.4\\ 2\cdot7\pm0.6\\ 5\cdot1\pm3\cdot1\ (2\cdot6)\\ 0\cdot5\pm1\cdot3\ (1\cdot3)\\ 1\cdot5\pm0.7\ (1\cdot3)\\ 3\cdot9\pm0.7\ (2\cdot5)\\ 2\cdot2\pm0\cdot3\ (2\cdot2)\\ 1\cdot8\pm0\cdot3\ (2\cdot2)\end{array}$	0.624 ± 2 0.730 ± 2 0.694 ± 2 0.532 ± 3	0.219 ± 2 0.222 ± 2 0.064 ± 2 0.203 ± 4	0.181 ± 2 0.993 ± 3 0.514 ± 2 0.555 ± 3			
$O_s(2) O_w(1) O_w(2)$	$\begin{array}{c} 5.9 \pm 0.7 & (2.2) \\ 2.2 \pm 0.3 & (2.2) \\ 1.8 \pm 0.3 & (2.2) \\ 1.9 \pm 0.2 & (1.9) \end{array}$						

Discussion

The interatomic distances and bond angles are given in Table 7. The errors were computed by using the entire variance-covariance matrix and include the trivial effect of lattice constant error. However, the errors in distances and angles involving hydrogen assume no error in the heavy atom positions. The anisotropic thermal parameters were transformed to obtain the thermal ellipsoid parameters which are given in Table 8.

The isotropic thermal parameters computed from the neutron data, except those for cesium and aluminum, are in good agreement with the isotropic parameters (Table 5) equivalent to the anisotropic parameters obtained from the X-ray data (Hamilton, 1959). The reason for the two exceptions is that cesium and aluminum are distinguished in projection only by their different scattering lengths and their different thermal parameters. Therefore the correlation between B_{CS} and B_{A1} is large (-0.82) and is manifest in the relatively large standard deviations of these two parameters.

The octahedron about aluminum is oriented almost exactly along the cell axes and is only very slightly distorted. The Cs-O_s(2) distances are a little longer than the Cs-O_w(1) distances, 3.454 Å vs 3.367 Å. The analogous distances in MASD are 3.42 Å to O_s(2) and 3.61 Å to O_w(1).

The sulfate group is an almost perfect tetrahedron. Rigid body analysis of the sulfate group was carried out by the method of Cruickshank (1956) using a code written by Trueblood (1962). The τ and ω matrices are in Table 9. Corrections to the S–O distances were computed according to the in phase assumption of Busing & Levy (1964). The S–O distances before and after correction are given in Table 7. These distance agree well with other recent accurate determinations which have been tabulated by Larson (1965). The direction of maximum motion of $O_s(1)$ is normal to the S–O bond. The largest axis of the $O_s(2)$ thermal ellipsoid makes an angle of 85.7° with the S–O bond and the smallest axis makes an angle of 9.1° with the bond.

There is only one possible system of hydrogen bonding in this structure. All hydrogen atoms take part in hydrogen bonds and all oxygen atoms except $O_w(2)$ have at least one hydrogen bond. The hydrogen positions could be reasonably guessed from the heavy-atom locations obtained by X-rays. Hydrogen atoms could be clearly observed in a three-dimensional difference Fourier synthesis computed with reflections having $\sin \theta/\lambda < 0.4 \text{ Å}^{-1}$. The O–H bond lengths were corrected for thermal motion according to Busing & Levy (1964) by using the isotropic thermal parameters obtained from the neutron diffraction data. These distances, before and after being corrected, are given in Table 7 and agree well with other neutron diffraction analyses of hydrated crystals. H(1) on $O_w(1)$ is bonded to $O_s(1)$ and this oxygen atom, being on a threefold axis, is bonded to three H(1) atoms. A somewhat elongated trigonal pyramid consisting of the three hydrogen

Table 6. Observed and calculated neutron diffraction structure factors, $\times 100$, for CsAl(SO₄)₂. 12H₂O

				of is nega	the the him	ius sign inc	ans 1033 (
k	$ F_o $	F_c	k	$ F_o $	Fc	k	$ F_o $	F_{c}	k	$ F_o $	F_{c}
	h=2			h=6			h = 10			h = 14	
0	215	172	0	1217	1156	0	900	-975	0	758	890
1	913	908	1	- 342	80	1	-431	362	1	684	580
2	913	919	2	2757	2744	2	440	495	2	- 502	261
3	- 286	- 98	3	600	- 686	3	564	-614	3	- 500	227
4	413	400	4	694	728	4	802	-654	4	-431	-277
5	830	813	5	383	- 397	5	- 380	-122	5	624	546
6	- 336	179	6	1753	1686	6	1584	1584	6	703	737
7	-350	314	7	419	-456	7	471	- 485	7	364	334
8	672	701	8	512	325	8	814	924	8	398	385
9	- 367	- 550	9	385	- 431	9	- 468	289			
10	871	935	10	-412	279	10	- 397	201			
11	783	- 743	11	-419	- 486	11	- 464	443			
12	- 389	-175	12	875	934	12	- 466	697			
13	499	- 512	13	-428	79	13	-415	107			
14	1017	1110	14	640	554						
15	-403	-253	15	-421	-212						
16	- 439	244									
	h = 4			h = 8			h = 12			h=16	
0	-311	31	0	560	680	0	1558	1512	0	537	- 384
1	565	- 528	1	- 392	-269	1	606	- 556	1	-463	-248
2	505	- 493	2	2284	2304	2	1198	1265	2	568	- 529
3	494	- 510	3	973	1039	3	- 399	179	3	-454	-9
4	450	-530	4	- 397	- 76	4	861	813	4	466	303
5	879	-875	5	547	528	5	-476	23			
6	845	836	6	1040	1002	6	455	377			
7	1177	- 1089	7	554	560	7	-473	166			
8	1241	1310	8	921	957	8	-412	-51			
9	- 385	126	9	-426	115	9	395	148			
10	387	- 461	10	- 387	- 306	10	- 396	5			
11	- 393	266	11	421	-455	11	- 399	174			
12	936	816	12	848	860						
13	-403	- 78	13	- 443	-132						
14	416	355	14	- 428	141						
15	-413	80									
16	580	-616									

If $|F_o|$ is negative the minus sign means 'less than'

Table 7. Interatomic distances and angles in CsAl(SO₄)₂. 12H₂O from fixed crystal and neutron diffraction data Standard deviations, in parentheses, apply to the rightmost digit Distances corrected for thermal motion are in parentheses

$Al-6O_w(2)$	1·882 (5) Å		
$\begin{array}{c} \text{Cs-6O}_w(1) \\ -6\text{O}_s(2) \end{array}$	3·367 (5) 3·454 (5)		
The sulfate group			
S-O ₈ (1)	1.479 (9)	$< O_s(1) - S - O_s(2)$	109·9 (2)°
5 20 (2)	(1.496)	$$	109.0 (2)
S−3O ₈ (2)	1.473(5)	$< O_s(2) - O_s(2) - O_s(2)$	60·0
$O_{2}(1) - 3O_{2}(2)$	(1.465) 2.417 (8)	$< O_{s}(2) - O_{s}(2) - O_{s}(1)$	60.2(1)
$O_s(2) - 2O_s(2)$	2.399 (8)	$< O_{s}(2) - O_{s}(1) - O_{s}(2)$	39-3 (3)
Water molecules			
$O_w(1) - H(1)$	0.941 (26)	$< H(1) - O_w(1) - H(2)$	107.6 (24)
0 (1) YY (0)	(0.955)		· · /
$O_w(1) - H(2)$	0.963(29)		
$O_{1}(2) = H(3)$	(0.908) 0.974 (26)	$< H(2) \cap (1) H(4)$	107.2 (20)
$O_w(2)$ $\Pi(3)$	(0.974)	$< H(3) - O_w(1) - H(4)$	107-2 (20)
$O_w(2) - H(4)$	0.984 (36)		
	(0.995)		
Hydrogen bonds			
$O_s(1) - 3O_w(1)$	2.822 (6)	$< O_{s}(1) - H(1) - O_{w}(1)$	165 (2)
$O_{s}(1) - 3H(1)$	1.902 (25)		100 (2)
$O_s(2) - O_w(1)$	2.766 (7)	$< O_{2}(2) - H(2) - O_{2}(1)$	171 (3)
$O_{s}(2) - H(2)$	1.811 (29)		1/1 (5)
$O_s(2) - O_w(2)$	2.648 (7)	$< O_{s}(2) - H(3) - O_{s}(2)$	166 (3)
$O_s(2) - H(3)$	1.692 (27)		100 (5)
$O_w(1) - O_w(2)$	2.615 (7)	$< \Omega_{\rm m}(1) - H(4) - \Omega_{\rm m}(2)$	163 (3)
$O_w(1) - H(4)$	1.657 (33)		105 (5)
Miscellaneous angles	5		
$Al-O_w(2)-H(3)$	121 (2)°	< H(1)–O ₈ (1)–H(1)	102 (1)
$Al-O_w(2)-H(4)$	130 (2)	$< H(1) - O_{\delta}(1) - S$	116 (1)
$H(3) - O_w(2) - H(4)$	107 (2)		
$H(1)-O_w(1)-H(4)$	109 (2)	< H(2)–O _s (2)–H(3)	101 (1)
$H(2) - O_w(1) - H(4)$	116 (2)	$< S-O_s(2)-H(2)$	119 (1)
$H(1) - O_w(1) - H(2)$	108 (3)	$< S-O_s(2)-H(3)$	131 (1)

Table 8. Thermal ellipsoids in $CsAl(SO_4)_2$. $12H_2O$, fixed crystal data

	r.m.s.		Direction an	gles relative to	o crystal axes
Atom	amplitude	B_i	α	β	γ
Cs	0·162±3 Å	2·08 ± 7 Ų	54·7°	54·7°	54·7°
	0.191 ± 2	2.88 ± 5			
	0.191 ± 2	2.88 <u>+</u> 5	_	_	
Al	0.145 ± 11	1.66 ± 25	54.7	54.7	54.7
	0.122 ± 7	1.17 ± 14			
	0.122 ± 7	1.17 ± 14	_		_
S	0.146 ± 7	1.68 ± 15	54.7	54.7	54.7
	0.120 ± 5	1.14 ± 9	_		_
	0.120 ± 5	1·14±9	—		
$O_s(1)$	0.119 + 22	1.11 + 42	54.7	54.7	54.7
	0.199 ± 10	3.13 + 32	_	547	547
	0.199 ± 10	3.13 ± 32	_		
O _s (2)	0.214 ± 9	3.63 + 29	33 + 5	72 + 7	64 + 4
	0.155 ± 10	1.91 ± 25	108 ± 9	19 + 7	95 ± 13
	0.118 ± 12	1.10 ± 23	116 ± 6	93 ± 13	26 ± 5
$O_w(1)$	0.150 ± 10	1.78 ± 25	28 + 14	89 + 28	118 + 13
	0.168 ± 9	2.22 ± 25	96 ± 28	11 + 28	99 + 28
	0·183±9	2.66 ± 27	63 ± 13	79 ± 27	30 ± 14
$O_w(2)$	0.120 ± 11	1.15 ± 21	16+9	98 + 14	104 + 8
	0·160 <u>+</u> 9	2.02 ± 23	83 ± 15	8 ± 14	94 + 22
	0·178±9	2.51 ± 26	76 ± 8	88 ± 22	14 ± 10

•

Table 9. Translation and torsional vibration matrices for the sulfate group relative to the unit cell axes

$$\tau = \begin{pmatrix} 0.0160 & 0.0015 & 0.0015 \\ 0.0160 & 0.0015 \\ 0.0160 \end{pmatrix} \overset{}{A^2} \qquad \omega = \begin{pmatrix} 29.2 & -8.8 & -8.8 \\ 29.2 & -8.8 \\ 29.2 \end{pmatrix} deg$$

$$\sigma \tau = \begin{pmatrix} 0.0020 & 0.0017 & 0.0017 \\ 0.0020 & 0.0017 \\ 0.0020 \end{pmatrix} \overset{}{A^2} \qquad \sigma \omega = \begin{pmatrix} 5.1 & 3.9 & 3.9 \\ 5.1 & 3.9 \\ 5.1 \end{pmatrix} deg$$

atoms and the sulfur atom thus surrounds O(1). H(2)on $O_w(1)$ and H(3) on $O_w(2)$ are bonded to $O_s(2)$. These hydrogen atoms and the sulfur atom are nearly coplanar with $O_s(2)$. H(4) on $O_w(2)$ is bonded to $O_w(1)$. The angles involving H(1), H(2) and H(4) about $O_w(1)$ are nearly tetrahedral.

Hamilton (1962) has given an empirical relation between O-O hydrogen bond lengths and O-H bond lengths or O-H---O angles. His empirical functions and the present experimental values are plotted in Fig. 2. The present O-H distances are systematically smaller than predicted but the differences are within the standard deviation of the measurement and the standard deviation of the prediction of the empirical function. There is no systematic trend in the O-H---O angles, all of which are nonlinear, but again the differences between the present experimental values and the empirical curve are not significant.



Fig.2. Plot of O-H distance vs O-O, the hydrogen bond distance (circles) and O-H---O angle vs O-O distance (triangles). The upper line is the empirical function for O-H distance and the lower line is the empirical function for O-H---O angle (Hamilton, 1962).

ω= (29.2	8·8 29·2	$\begin{pmatrix} -8.8 \\ -8.8 \\ 29.2 \end{pmatrix}$	deg ²
$\sigma \omega = \left(\right)$	5.1	3·9 5·1	3·9 3·9 5·1	deg ²

Although the present results are of considerably greater accuracy than those of Lipson (1935), the maximum shift in atomic position is only 0.04 Å.

Except as noted, all calculations were performed on an IBM 7094 computer using codes written by Larson. Roof & Cromer (1963, 1964, 1965). Fig.1 was drawn by an SC-4020 microfilm plotter.

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