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# Neutron Diffraction Study of the Space Group and Structure of Manganese-Leonite, $K_2Mn(SO_4)_2.4H_2O$

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A total of 542 neutron reflexions – three-dimensional up to $(\sin\theta)/\lambda \sim 0{\cdot}40$ and in three zones, $h0l$, $hk0$ and $0kl$, up to $(\sin\theta)/\lambda \sim 0{\cdot}70$ – have been used to refine the structure of $K_2Mn(SO_4)_2.4H_2O$ in the space group $C2/m$ to an $R$ value of 0·092. One of the two non-equivalent sulphate groups appears to be disordered. All the hydrogen atoms of the water molecules are involved in normal O–H---O hydrogen bonds. The water molecule $H_2O_w(1)$ has a tetrahedral coordination; one of its lone pair orbitals is directed toward a potassium ion and the other toward a manganese ion. For the other two water molecules, $H_2O_w(2)$ and $H_2O_w(3)$, the bisectors of their lone-pair orbitals are directed toward manganese ions. In addition, $O_w(2)$ has two potassium-ion neighbours at 3·09 Å nearly normal to the plane of the water molecule leading to an approximately trigonal bipyramidal coordination for $H_2O_w(2)$. Refinements of the structure in the alternative space groups $C2$ and $Cm$ have provided no justification for choosing either of them in preference to $C2/m$.

## Introduction

The crystal structure originally proposed by Anspach (1939) for $K_2Mn(SO_4)_2.4H_2O$ was criticized by Wyckoff (1957) for its 'improbably short K–O separations of 2·28 Å'. The problem was reinvestigated with the use of $h0l$ and $hk0$ X-ray data by Schneider (1961) who found a completely different but satisfactory structure for the crystal in the space group $C2/m$. However, in the absence of a determination of the hydrogen positions, no hydrogen-bonding scheme for the water molecules was proposed and, further, the possibility of a lower space group symmetry was suspected. A neutron-diffraction study of this structure was therefore undertaken as part of our continuing investigations of hydrogen-bonded hydrate crystals.

## Experimental

Large crystals of monoclinic $K_2Mn(SO_4)_2.4H_2O$ could be grown by evaporating at room temperature a saturated aqueous solution containing equimolecular proportions of potassium sulphate and manganous sulphate. All the crystals obtained were twinned across the (100) plane but good single crystals could be separated out by grinding. The neutron Bragg angles recorded by us were found to be consistent with the unit-cell constants given by Schneider (1961), *viz.*

$$a=12{\cdot}03\pm0{\cdot}03,\ b=9{\cdot}61\pm0{\cdot}03,\ c=9{\cdot}98\pm0{\cdot}04\ \text{Å},\quad \beta=95{\cdot}0\pm0{\cdot}3^\circ,$$

which were therefore used subsequently in our bond-length and bond-angle calculations.

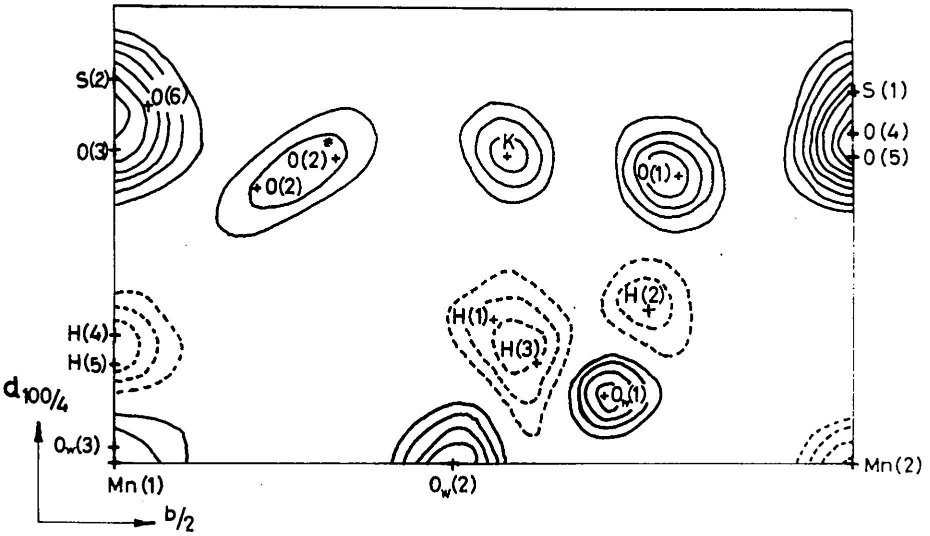

Fig. 1. Projection of the nuclear scattering density along [001]. The contours are at intervals of $0{\cdot}5\times10^{-12}$ cm.Å$^{-2}$. The negative contours are shown by broken lines and the zero contour by dot-dash lines.

All the measurements were made at the Cirus reactor in Trombay. The *h*0*l* and *hk*0 data were collected at a wavelength of 0·953 Å up to $(\sin\theta)/\lambda \sim 0{\cdot}70$ from cylindrical crystals of diameter 1·5 mm and weights 0·082 and 0·062 g respectively in the semi-automatic diffractometer SAND (Chidambaram, Sequeira & Momin, 1967). Three-dimensional data up to $(\sin\theta)/\lambda \sim 0{\cdot}40$ were recorded at 1·031 Å on the diffractometer DCD (Chidambaram, Sequeira & Sikka, 1964) with a General Electric Single Crystal Orienter using a cylindrical sample of diameter 1·5 mm (weight 0·034 g), its length of 6 mm being parallel to the *c* axis of the crystal and the $\varphi$ axis of the orienter. The latter measurements were extended for the 0*kl* data alone up to $(\sin\theta)/\lambda \sim 0{\cdot}70$. A total of 542 reflexions were thus recorded.*

The linear absorption coefficient was measured and found to be 1·25 $\text{cm}^{-1}$ and the absorption corrections to the data were applied with use of the program ORABS† (Wehe, Busing & Levy, 1962).

## Analysis and refinement of the structure: choice of space group

The *h*0*l* data were first reduced to absolute scale by the method of Wilson (1949). A Fourier plot of the projection of nuclear scattering density along [010] was made with the phases given by the heavy-atom positions as determined by Schneider (1961). The negative peaks in this plot could be identified as the manganese and hydrogen atoms. Analysis of the *hk*0 data in a similar fashion gave the *x* and *y* coordinates of the hydrogen atoms. All the 542 pieces of data were then combined and a full-matrix least-squares refinement of the structure on *F* was carried out with individual isotropic temperature factors and unit weights for all the reflexions by means of the program ORFLS (Busing, Martin & Levy, 1962). After several cycles, the *R* index, $(\Sigma\,||F_o|-|F_c||)/\Sigma\,|F_o|$, converged to 0·174. It was found at this stage that the average $\langle||F_o|-|F_c||\rangle$ could be represented as $0{\cdot}52+0{\cdot}003|F_o|^2$. Hence a weighting scheme

$$w=(0{\cdot}52+0{\cdot}003|F_o|^2)^{-2}$$

was used and the refinement then converged at an *R* value of 0·167.

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* About a dozen more reflexions which were later discovered to have been recorded during a short period of 'bad electronics' were omitted from the analysis.

† All the calculations in this article were carried out on the CDC-3600 computer in the Tata Institute of Fundamental Research, Bombay.

Table 1. *Comparison of isotropic least-squares refinements in the various space groups*

| Space group | Number of parameters varied, *m* | *R* | Ratio of *R*'s [relative to *C*2/*m* (ord.)] | Dimension of the hypothesis*, *b* | Degrees of freedom *n*−*m* | $\mathscr{R}_{b,\,n-m,0.005}$† |
|---|---|---|---|---|---|---|
| *C*2/*m* (ordered) | 63 | 0·1673 | | | | |
| *C*2 | 103 | 0·1390 | 1·203 | 40 | 439 | 1·076 |
| *Cm* | 122 | 0·1470 | 1·138 | 59 | 420 | 1·107 |
| *C*2/*m* (disordered) | 68 | 0·1347 | 1·242 | 5 | 474 | 1·018 |

* Notation of Hamilton (1964).

† The limiting value for the significance level of 0·5%. That is, if the ratio in column 4 exceeds this value, the space group *C*2/*m* (ord.) can be rejected in favour of the space group in column 1 at this significance level. See Hamilton (1964, 1965).

Table 2. *Results of anisotropic least-squares refinement* in the various space groups*

| Space group | Number of parameters, *m* | *R* | Ratio of *R*'s: relative to | Ratio of *R*'s: Ratio value | Dimension of the hypothesis, *b* | Degrees of freedom *n*−*m* | $\mathscr{R}_{b,\,n-m,\alpha}$: $\alpha=0{\cdot}005$ | $\mathscr{R}_{b,\,n-m,\alpha}$: $\alpha=0{\cdot}25$ |
|---|---|---|---|---|---|---|---|---|
| *C*2/*m* (ordered) | 134 | 0·0997 | | | | | | |
| *C*2/*m* (disordered) | 146 | 0·0924 | *C*2/*m* (ord.) | 1·079 | 12 | 396 | 1·036 | 1·018 |
| *C*2 | 230 | 0·0812 | *C*2/*m* (disord.) | 1·138 | 84† | 312 | 1·190 | 1·141 |
| *Cm* | 257 | 0·0776 | *C*2/*m* (disord.) | 1·191 | 111† | 285 | 1·253 | 1·197 |

* The weighting scheme used in the final stages of the refinement was $w=(0{\cdot}3+0{\cdot}0009\,|F_o|^2)^{-2}$.

† Strictly speaking, comparison of *C*2 or *Cm* and *C*2/*m* (disordered) is perhaps not justified since the degrees of freedom involved in the disorder of the sulphate group in the latter are not fully available in the former. But the error in $\mathscr{R}$ on this account is likely to be negligible for our purpose.

Table 3. *Ranges of bond-length and bond-angle values in the various least-squares refinements*

| Parameter | *C*2 | *Cm* | *C*2/*m* (disordered) |
|---|---|---|---|
| S–O | 1·349 – 1·523 Å | 1·324 – 1·538 Å | 1·420 – 1·530 Å |
| ∠O–S–O | 103·7 – 115·8° | 98·1 – 119·2° | 105·1 – 113·4° |
| $O_w$–H | 0·867 – 1·090 Å | 0·817 – 1·053 Å | 0·908 – 0·994 Å |
| ∠H–$O_w$–H | 103·8 – 111·4° | 100·9 – 108·9° | 104·4 – 108·8° |

Table 4. *Positional and thermal parameters in* $K_2Mn(SO_4)_2.4H_2O$

The expression for the Debye–Waller factor is $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$.
The least-squares standard errors are given in parentheses.

| | Fractional coordinate × $10^4$ | | | Thermal parameter × $10^4$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
| K | 1695 (5) | 2632 (8) | 2492 (7) | 26 (3) | 35 (7) | 55 (6) | −8 (5) | 0 (4) | −20 (12) |
| Mn(1) | 0 | 0 | 0 | 19 (8) | 0 (11) | 74 (20) | 0 | 0 (15) | 0 |
| Mn(2) | 0 | 5000 | 5000 | 16 (6) | 31 (12) | 52 (13) | 0 | −3 (9) | 0 |
| S(1) | 2065 (8) | 5000 | −414 (11) | 14 (6) | 32 (11) | 21 (9) | 0 | 7 (8) | 0 |
| S(2) | 2130 (11) | 0 | −4810 (15) | 15 (6) | 75 (20) | 62 (14) | 0 | −10 (10) | 0 |
| O(1) | 1587 (3) | 3750 (6) | −1136 (4) | 39 (3) | 52 (5) | 40 (3) | −11 (4) | 7 (2) | −16 (6) |
| O(2) | 1509 (13) | 970 (16) | −4005 (15) | 32 (7) | 64 (15) | 95 (15) | 13 (10) | 7 (9) | −23 (22) |
| O(2)* | 1704 (13) | 1442 (16) | −4454 (17) | 32 (8) | 71 (17) | 135 (25) | 17 (9) | −1 (13) | −21 (22) |
| O(3) | 1730 (5) | 0 | 570 (10) | 13 (3) | 91 (13) | 110 (13) | 0 | 14 (6) | 0 |
| O(4) | 1817 (8) | 5000 | 951 (8) | 71 (6) | 72 (10) | 30 (6) | 0 | 23 (5) | 0 |
| O(5) | 1692 (5) | 5000 | 4336 (8) | 14 (3) | 60 (9) | 55 (7) | 0 | 5 (4) | 0 |
| O(6) | 1935 (6) | 233 (15) | 3744 (8) | 39 (5) | 41 (16) | 42 (6) | −14 (9) | 2 (5) | −39 (13) |
| $O_w(1)$ | 397 (4) | 3346 (6) | −3521 (4) | 28 (2) | 34 (5) | 34 (4) | 2 (3) | 7 (3) | 9 (6) |
| $O_w(2)$ | 0 | 2277 (8) | 0 | 44 (5) | 33 (7) | 129 (13) | 0 | 23 (9) | 0 |
| $O_w(3)$ | 90 (8) | 0 | −2219 (8) | 45 (6) | 89 (14) | 44 (6) | 0 | 16 (6) | 0 |
| H(1) | 779 (8) | 2549 (12) | −3845 (9) | 60 (7) | 63 (10) | 79 (9) | 8 (8) | 4 (7) | −18 (17) |
| H(2) | 848 (7) | 3617 (10) | −2699 (9) | 50 (5) | 62 (10) | 60 (7) | 12 (7) | −1 (6) | 8 (12) |
| H(3) | 562 (8) | 2896 (13) | −367 (10) | 51 (5) | 62 (13) | 101 (9) | −7 (9) | 1 (6) | 9 (13) |
| H(4) | 698 (16) | 0 | −2755 (23) | 66 (13) | 139 (28) | 135 (28) | 0 | 8 (18) | 0 |
| H(5) | 554 (14) | 0 | 2766 (15) | 71 (11) | 115 (23) | 74 (14) | 0 | −2 (12) | 0 |

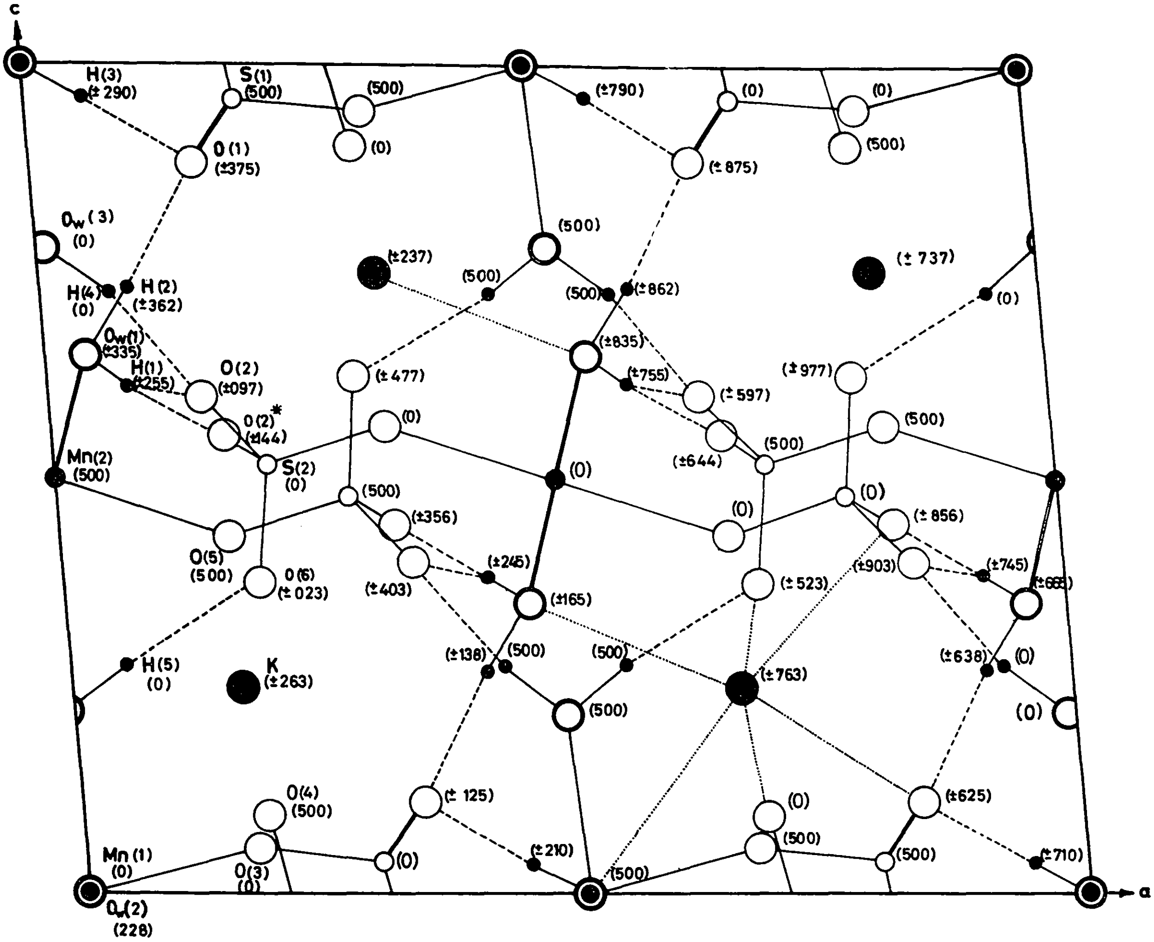

Fig. 2. Schematic projection of the structure along [010]. The fractional $y$ coordinates ($\times 10^3$) of the atoms are given in parentheses.

Table 5. $K_2Mn(SO_4)_2.4H_2O$: *observed and calculated structure factors*

The nuclear scattering lengths used are (in units of $10^{-12}$ cm): potassium 0·35; manganese −0·37; sulphur 0·31; oxygen 0·58; hydrogen −0·378. The four columns in each set contain respectively the Miller indices *h* and *l*, 100 $|F_o|$ and 100 $F_c$.

| | | | |
|---|---|---|---|
| H 0 L | | | |
| 0 | 1 | 0 | -9 |
| 0 | 2 | 636 | 656 |
| 0 | 3 | 278 | -260 |
| 0 | 4 | 937 | -987 |
| 0 | 5 | 160 | 156 |
| 0 | 6 | 379 | -367 |
| 0 | 7 | 735 | -718 |
| 0 | 8 | 257 | 272 |
| 0 | 9 | 1189 | 1197 |
| 0 | 10 | 254 | -259 |
| 0 | 11 | 0 | 65 |
| 0 | 12 | 14 | -31 |
| 0 | 13 | 236 | -246 |
| 0 | 14 | 16 | -46 |
| 2 | 0 | 1246 | -1351 |
| 2 | 1 | 343 | -363 |
| 2 | 2 | 398 | -410 |
| 2 | 3 | 447 | 491 |
| 2 | 4 | 449 | -469 |
| 2 | 5 | 263 | -296 |
| 2 | 6 | 420 | 391 |
| 2 | 7 | 192 | -229 |
| 2 | 8 | 664 | -632 |
| 2 | 9 | 689 | 596 |
| 2 | 10 | 219 | 224 |
| 2 | 11 | 240 | [illegible] |
| 2 | 12 | 268 | 218 |
| 2 | 13 | 34 | 61 |
| 2 | 14 | 127 | 131 |
| -2 | 1 | 394 | 382 |
| -2 | 2 | 653 | -695 |
| -2 | 3 | 200 | -226 |
| -2 | 4 | 173 | 178 |
| -2 | 5 | 1232 | 1274 |
| -2 | 6 | 1230 | 1261 |
| -2 | 7 | 603 | -601 |
| -2 | 8 | 389 | 314 |
| -2 | 9 | 617 | 668 |
| -2 | 10 | 611 | -673 |
| -2 | 11 | 390 | -315 |
| -2 | 12 | 99 | 108 |
| -2 | 13 | 243 | 203 |
| -2 | 14 | 696 | 810 |
| 4 | 0 | 0 | 6 |
| 4 | 1 | 165 | 72 |
| 4 | 2 | 716 | -725 |
| 4 | 3 | 235 | 260 |
| 4 | 4 | 452 | 459 |
| 4 | 5 | 25 | 14 |
| 4 | 6 | 806 | 831 |
| 4 | 7 | 497 | -475 |
| 4 | 8 | 539 | -560 |
| 4 | 9 | 122 | -105 |
| 4 | 10 | 444 | -398 |
| 4 | 11 | 560 | -539 |
| 4 | 12 | 100 | 96 |
| 4 | 13 | 41 | -59 |
| 4 | 14 | 571 | 510 |
| -4 | 1 | 212 | -220 |
| -4 | 2 | 171 | -137 |
| -4 | 3 | 822 | 777 |
| -4 | 4 | 204 | 209 |
| -4 | 5 | 771 | 730 |
| -4 | 6 | 144 | 100 |
| -4 | 7 | 291 | -344 |
| -4 | 8 | 865 | 840 |
| -4 | 9 | 66 | -31 |
| -4 | 10 | 65 | -59 |
| -4 | 11 | 861 | 831 |
| -4 | 12 | 354 | -338 |
| -4 | 13 | 354 | 238 |
| 6 | 0 | 2597 | 2757 |
| 6 | 1 | 138 | 187 |
| 6 | 2 | 443 | -400 |
| 6 | 3 | 191 | -88 |
| 6 | 4 | 37 | -57 |
| 6 | 5 | 65 | -63 |
| 6 | 6 | 1207 | -1149 |
| 6 | 7 | 663 | 686 |
| 6 | 8 | 91 | 76 |
| 6 | 9 | 385 | 429 |
| 6 | 10 | 133 | -113 |
| 6 | 11 | 60 | -74 |
| 6 | 12 | 49 | -62 |
| 6 | 13 | 273 | -304 |
| 6 | 14 | 396 | -424 |
| -6 | 1 | 159 | 102 |
| -6 | 2 | 409 | 375 |
| -6 | 3 | 750 | 781 |
| -6 | 4 | 145 | -158 |
| -6 | 5 | 381 | 344 |
| -6 | 6 | 1171 | -1243 |
| -6 | 7 | 281 | -240 |
| -6 | 8 | 945 | 836 |
| -6 | 9 | 65 | -78 |
| -6 | 10 | 25 | 35 |
| -6 | 11 | 578 | 567 |
| -6 | 12 | 318 | -317 |
| -6 | 13 | 11 | 24 |
| 8 | 0 | 278 | -291 |
| 8 | 1 | 1134 | 1085 |
| 8 | 2 | 864 | -910 |
| 8 | 3 | 472 | 491 |
| 8 | 4 | 459 | 499 |
| 8 | 5 | 498 | -521 |
| 8 | 6 | 43 | -56 |
| 8 | 7 | 258 | -255 |
| -8 | 8 | 297 | -223 |
| 8 | 9 | 41 | -64 |
| 8 | 10 | 153 | 126 |
| 8 | 11 | 78 | 91 |
| -8 | 1 | 437 | -437 |
| -8 | 2 | 113 | 141 |
| -8 | 3 | 134 | -25 |
| -8 | 4 | 502 | 507 |
| -8 | 5 | 1191 | 1258 |
| -8 | 6 | 249 | 209 |
| -8 | 7 | 1094 | 1049 |
| -8 | 8 | 324 | 378 |
| -8 | 9 | 392 | -349 |
| -8 | 10 | 304 | 301 |
| -8 | 11 | 590 | -550 |
| -8 | 12 | 502 | -523 |
| -8 | 13 | 502 | 348 |
| 10 | 0 | 304 | -297 |
| 10 | 1 | 1295 | 1346 |
| 10 | 2 | 239 | -190 |
| 10 | 3 | 170 | 185 |
| 10 | 4 | 856 | 874 |
| 10 | 5 | 640 | 657 |
| 10 | 6 | 628 | 587 |
| 10 | 7 | 207 | -234 |
| 10 | 8 | 230 | -195 |
| 10 | 9 | 43 | 38 |
| 10 | 10 | 210 | -192 |
| 10 | 11 | 376 | -373 |
| -10 | 1 | 412 | -368 |
| -10 | 2 | 595 | 569 |
| -10 | 3 | 39 | 65 |
| -10 | 4 | 334 | 363 |
| -10 | 5 | 228 | -134 |
| -10 | 6 | 343 | -383 |
| -10 | 7 | 21 | 56 |
| -10 | 8 | 204 | -197 |
| -10 | 9 | 484 | -520 |
| -10 | 10 | 270 | 294 |
| -10 | 12 | 372 | -340 |
| 12 | 0 | 306 | 342 |
| 12 | 1 | 316 | 312 |
| 12 | 2 | 247 | 203 |
| 12 | 3 | 748 | -754 |
| 12 | 4 | 168 | 151 |
| 12 | 5 | 132 | 137 |
| 12 | 6 | 519 | -515 |
| 12 | 7 | 745 | 773 |
| 12 | 8 | 212 | -232 |
| 12 | 9 | 509 | 470 |
| -12 | 1 | 751 | 772 |
| -12 | 2 | 360 | 300 |
| -12 | 3 | 125 | -85 |
| -12 | 4 | 291 | 277 |
| -12 | 5 | 41 | -26 |
| -12 | 6 | 915 | -962 |
| -12 | 7 | 68 | 74 |
| -12 | 8 | 264 | -290 |
| 14 | 0 | 645 | -661 |
| 14 | 1 | 230 | 183 |
| 14 | 2 | 340 | 317 |
| 14 | 3 | 71 | 55 |
| 14 | 4 | 68 | 43 |
| 14 | 5 | 266 | -246 |
| 14 | 6 | 140 | 125 |
| -14 | 1 | 357 | 338 |
| -14 | 2 | 219 | -195 |
| -14 | 3 | 669 | -607 |
| -14 | 4 | 358 | 328 |
| -14 | 5 | 494 | 444 |
| 16 | 0 | 546 | -509 |
| 16 | 1 | 175 | 161 |
| 16 | 2 | 91 | 105 |
| -16 | 1 | 109 | 128 |
| -16 | 2 | 524 | -573 |
| 18 | 0 | 399 | 451 |
| H 1 L | | | |
| 1 | 0 | 43 | -33 |
| 1 | 1 | 125 | -142 |
| 1 | 2 | 301 | -317 |
| 1 | 3 | 330 | -307 |
| 1 | 4 | 215 | -151 |
| 1 | 5 | 915 | 894 |
| 1 | 6 | 664 | -584 |
| 1 | 7 | 325 | -274 |
| -1 | 1 | 103 | -127 |
| -1 | 2 | 502 | 469 |
| -1 | 3 | 201 | -167 |
| -1 | 4 | 1054 | 1060 |
| -1 | 5 | 68 | -36 |
| -1 | 6 | 285 | 392 |
| -1 | 7 | 113 | -256 |
| 3 | 0 | 57 | 53 |
| 3 | 1 | 745 | 785 |
| 3 | 2 | 118 | -87 |
| 3 | 3 | 922 | -888 |
| 3 | 4 | 90 | 153 |
| 3 | 5 | 196 | -63 |
| 3 | 6 | 180 | -185 |
| 3 | 7 | 0 | 25 |
| -3 | 1 | 480 | 484 |
| -3 | 2 | 33 | -24 |
| -3 | 3 | 648 | -631 |
| -3 | 4 | 0 | -8 |
| -3 | 5 | 695 | -718 |
| -3 | 6 | 634 | -628 |
| 5 | 0 | 196 | 127 |
| 5 | 1 | 373 | -427 |
| 5 | 2 | 732 | 730 |
| 5 | 3 | 471 | -440 |
| 5 | 5 | 306 | 258 |
| 5 | 6 | 0 | 49 |
| -5 | 1 | 391 | -399 |
| -5 | 2 | 754 | -875 |
| -5 | 3 | 0 | 81 |
| -5 | 4 | 201 | -166 |
| -5 | 5 | 237 | 159 |
| -5 | 6 | 282 | 321 |
| 7 | 0 | 132 | 91 |
| 7 | 1 | 218 | -185 |
| 7 | 2 | 283 | -246 |
| 7 | 3 | 106 | 65 |
| -7 | 1 | 80 | 120 |
| -7 | 2 | 189 | -157 |
| -7 | 3 | 229 | 192 |
| -7 | 4 | 960 | 886 |
| -7 | 5 | 345 | -234 |
| 9 | 0 | 525 | 538 |
| 9 | 1 | 359 | -369 |
| -9 | 1 | 337 | -310 |
| -9 | 2 | 265 | -223 |
| -9 | 7 | 186 | -117 |
| 11 | 0 | 426 | 385 |
| 13 | 0 | 203 | 157 |
| 15 | 0 | 220 | 229 |
| 17 | 0 | 75 | 59 |
| 19 | 0 | 83 | -96 |
| H 2 L | | | |
| 0 | 0 | 789 | 838 |
| 0 | 1 | 61 | 44 |
| 0 | 2 | 840 | 823 |
| 0 | 3 | 180 | -112 |
| 0 | 4 | 766 | -774 |
| 0 | 5 | 362 | 408 |
| 0 | 6 | 467 | -591 |
| 0 | 7 | 460 | -539 |
| 0 | 8 | 323 | -384 |
| 0 | 9 | 248 | -241 |
| 0 | 11 | 243 | -309 |
| 0 | 13 | 99 | 172 |
| 2 | 0 | 733 | -762 |
| 2 | 1 | 169 | 138 |
| 2 | 2 | 741 | -750 |
| 2 | 3 | 920 | -915 |
| 2 | 4 | 0 | 70 |
| 2 | 5 | 514 | 460 |
| 2 | 6 | 0 | -141 |
| 2 | 7 | 146 | -178 |
| -2 | 1 | 135 | -93 |
| -2 | 2 | 613 | -622 |
| -2 | 3 | 25 | 67 |
| -2 | 4 | 0 | 179 |
| -2 | 5 | 174 | 109 |
| -2 | 6 | 562 | -608 |
| -2 | 7 | 84 | 66 |
| 4 | 0 | 386 | -331 |
| 4 | 1 | 349 | 236 |
| 4 | 2 | 605 | -590 |
| 4 | 3 | 560 | 532 |
| 4 | 4 | 340 | 342 |
| 4 | 5 | 0 | 60 |
| 4 | 6 | 21 | -18 |
| -4 | 1 | 281 | -293 |
| -4 | 2 | 623 | -592 |
| -4 | 4 | 139 | 175 |
| -4 | 5 | 385 | -344 |
| -4 | 6 | 496 | -522 |
| -4 | 7 | 0 | -102 |
| 6 | 0 | 53 | 17 |
| 6 | 1 | 175 | -164 |
| 6 | 2 | 259 | 209 |
| 6 | 3 | 555 | -505 |
| 6 | 4 | 447 | -386 |
| 6 | 5 | 333 | 380 |
| -6 | 1 | 167 | 112 |
| -6 | 2 | 507 | -517 |
| -6 | 3 | 109 | -65 |
| -6 | 4 | 455 | -413 |
| -6 | 5 | 910 | -850 |
| -6 | 6 | 550 | -511 |
| 8 | 0 | 735 | -702 |
| 8 | 1 | 384 | -391 |
| 8 | 2 | 885 | -933 |
| -8 | 1 | 366 | -352 |
| -8 | 2 | 1418 | -1433 |
| -8 | 3 | 294 | 290 |
| -8 | 4 | 315 | 332 |
| 10 | 0 | 205 | 235 |
| 12 | 0 | 0 | 12 |
| 14 | 0 | 68 | 70 |
| 16 | 0 | 80 | -62 |
| 18 | 0 | 0 | -36 |
| H 3 L | | | |
| 1 | 0 | 70 | -67 |
| 1 | 1 | 326 | -347 |
| 1 | 2 | 83 | 70 |
| 1 | 3 | 0 | 26 |
| 1 | 4 | 922 | -902 |
| 1 | 5 | 364 | -378 |
| 1 | 6 | 241 | -215 |
| -1 | 1 | 246 | -248 |
| -1 | 2 | 616 | -608 |
| -1 | 3 | 450 | -425 |
| -1 | 4 | 689 | -649 |
| -1 | 5 | 431 | 429 |
| 3 | 0 | 196 | 176 |
| 3 | 1 | 811 | -812 |
| 3 | 2 | 330 | -387 |
| 3 | 3 | 87 | 23 |
| 3 | 4 | 98 | -78 |
| 3 | 5 | 416 | -352 |
| 3 | 6 | 388 | 333 |
| -3 | 1 | 912 | -928 |
| -3 | 2 | 197 | 163 |
| -3 | 3 | 531 | -495 |
| -3 | 4 | 169 | -170 |
| -3 | 5 | 733 | 763 |
| -3 | 6 | 423 | -501 |
| 5 | 0 | 589 | 586 |
| 5 | 1 | 190 | -192 |
| 5 | 2 | 1374 | -1340 |
| 5 | 3 | 143 | -150 |
| 5 | 4 | 110 | 73 |
| 5 | 5 | 496 | -476 |
| -5 | 1 | 491 | -496 |
| -5 | 2 | 111 | 59 |
| -5 | 3 | 274 | 217 |
| -5 | 4 | 120 | 108 |
| -5 | 5 | 167 | 182 |
| -5 | 6 | 513 | -575 |
| 7 | 0 | 411 | 485 |
| 7 | 1 | 1084 | 1060 |
| 7 | 2 | 682 | -639 |
| -7 | 1 | 100 | 56 |
| -7 | 2 | 374 | -321 |
| -7 | 3 | 108 | -70 |
| -7 | 4 | 250 | 231 |
| 9 | 0 | 150 | 123 |
| 11 | 0 | 308 | -341 |
| 13 | 0 | 321 | -310 |
| 15 | 0 | 241 | -224 |
| 17 | 0 | 127 | -137 |
| H 4 L | | | |
| 0 | 0 | 179 | 109 |
| 0 | 1 | 429 | 436 |
| 0 | 2 | 187 | -179 |
| 0 | 3 | 96 | -66 |
| 0 | 4 | 1074 | 1076 |
| 0 | 5 | 203 | 194 |
| 0 | 6 | 418 | -471 |
| 0 | 9 | 191 | -146 |
| 2 | 0 | 747 | -771 |
| 2 | 2 | 169 | -197 |
| 2 | 3 | 1762 | -1764 |
| 2 | 4 | 262 | 220 |
| 2 | 5 | 114 | 105 |
| -2 | 1 | 1176 | 1229 |
| -2 | 2 | 560 | -400 |
| -2 | 3 | 852 | 817 |
| -2 | 4 | 150 | 116 |
| -2 | 6 | 0 | 33 |
| 4 | 0 | 373 | 359 |
| 4 | 1 | 1009 | 941 |
| 4 | 2 | 450 | 585 |
| 4 | 3 | 165 | 2 |
| 4 | 4 | 473 | -444 |
| 4 | 5 | 871 | 816 |
| -4 | 1 | 547 | -550 |
| -4 | 2 | 158 | -141 |
| -4 | 3 | 414 | -429 |
| -4 | 4 | 157 | -144 |
| -4 | 5 | 331 | -340 |
| -4 | 6 | 485 | 642 |
| 6 | 0 | 569 | 546 |
| 6 | 2 | 250 | 239 |
| 6 | 3 | 311 | 301 |
| -6 | 1 | 316 | 359 |
| -6 | 3 | 776 | 609 |
| -6 | 4 | 550 | 560 |
| 8 | 0 | 139 | -90 |
| 10 | 0 | 1055 | 1057 |
| 12 | 0 | 203 | 186 |
| 14 | 0 | 216 | -227 |
| 16 | 0 | 100 | 143 |
| 18 | 0 | 121 | 103 |
| H 5 L | | | |
| 1 | 0 | 81 | 35 |
| 1 | 1 | 491 | 697 |
| 1 | 2 | 936 | 946 |
| 1 | 3 | 172 | -181 |
| 1 | 4 | 120 | 45 |
| 1 | 5 | 262 | 211 |
| -1 | 1 | 507 | 527 |
| -1 | 2 | 75 | -29 |
| -1 | 3 | 346 | -314 |
| -1 | 4 | 381 | 370 |
| -1 | 5 | 147 | 52 |
| 3 | 0 | 329 | 330 |
| 3 | 1 | 160 | -169 |
| 3 | 2 | 442 | 424 |
| 3 | 3 | 74 | 58 |
| 3 | 5 | 675 | 650 |
| -3 | 1 | 61 | -48 |
| -3 | 2 | 131 | -89 |
| -3 | 3 | 324 | -328 |
| -3 | 4 | 393 | 402 |
| -3 | 5 | 278 | 311 |
| 5 | 0 | 254 | 283 |
| 5 | 1 | 308 | -363 |
| 5 | 2 | 284 | -296 |
| -5 | 1 | 148 | 110 |
| -5 | 2 | 74 | -68 |
| -5 | 3 | 134 | -108 |
| -5 | 4 | 269 | 300 |
| 7 | 0 | 182 | 154 |
| 9 | 0 | 378 | 374 |
| 11 | 0 | 159 | 159 |
| 13 | 0 | 151 | 130 |
| 15 | 0 | 255 | 281 |
| 17 | 0 | 127 | 167 |
| H 6 L | | | |
| 0 | 0 | 900 | 856 |
| 0 | 1 | 408 | -398 |
| 0 | 2 | 636 | 566 |
| 0 | 3 | 179 | 117 |
| 0 | 4 | 1091 | -1025 |
| 0 | 7 | 1020 | -970 |
| 0 | 8 | 384 | -301 |
| 0 | 9 | 285 | 289 |
| 0 | 10 | 284 | -256 |
| 0 | 11 | 100 | 110 |
| 0 | 12 | 222 | -290 |
| 2 | 0 | 283 | -300 |
| 2 | 1 | 273 | -289 |
| 2 | 2 | 1079 | -1037 |
| 2 | 4 | 549 | -494 |
| -2 | 1 | 501 | -492 |
| -2 | 2 | 597 | -577 |
| -2 | 3 | 505 | 448 |
| -2 | 4 | 614 | -565 |
| 4 | 0 | 265 | 221 |
| 4 | 1 | 163 | 158 |
| 4 | 2 | 1134 | -1108 |
| -4 | 1 | 697 | -704 |
| -4 | 2 | 0 | -105 |
| -4 | 3 | 916 | -912 |
| 6 | 0 | 222 | 197 |
| 8 | 0 | 837 | -759 |
| 10 | 0 | 0 | 56 |
| 12 | 0 | 325 | -338 |
| 14 | 0 | 486 | -505 |
| 16 | 0 | 210 | -188 |
| H 7 L | | | |
| 1 | 0 | 520 | -536 |
| 1 | 1 | 635 | -615 |
| -1 | 1 | 329 | -263 |
| -1 | 2 | 279 | -272 |
| 3 | 0 | 180 | -201 |
| 3 | 1 | 0 | 68 |
| -3 | 1 | 0 | 0 |
| 5 | 0 | 164 | -99 |
| 7 | 0 | 57 | -41 |
| 9 | 0 | 403 | 389 |
| 11 | 0 | 408 | 397 |
| 13 | 0 | 150 | 52 |
| 15 | 0 | 113 | -43 |
| 17 | 0 | 40 | 38 |
| H 8 L | | | |
| 0 | 0 | 836 | 804 |
| 0 | 1 | 673 | 668 |
| 0 | 2 | 560 | 569 |
| 0 | 3 | 556 | -496 |
| 0 | 5 | 190 | -131 |
| 0 | 6 | 573 | -599 |
| 0 | 8 | 155 | -139 |
| 0 | 9 | 481 | 514 |
| 0 | 10 | 96 | 122 |
| 2 | 0 | 1027 | -1021 |
| 4 | 0 | 225 | -207 |
| 6 | 0 | 1267 | 1284 |
| 8 | 0 | 328 | -316 |
| 10 | 0 | 118 | -150 |
| 12 | 0 | 317 | 352 |
| 14 | 0 | 159 | -177 |
| 16 | 0 | 200 | -188 |
| H 9 L | | | |
| 1 | 0 | 470 | 459 |
| 3 | 0 | 1024 | 951 |
| 5 | 0 | 22 | 73 |
| 7 | 0 | 44 | -67 |
| 9 | 0 | 306 | 303 |
| 11 | 0 | 254 | -247 |
| 13 | 0 | 107 | -185 |
| 15 | 0 | 81 | 72 |
| H 10 L | | | |
| 0 | 0 | 201 | 190 |
| 0 | 3 | 274 | -240 |
| 0 | 4 | 369 | -344 |
| 0 | 5 | 180 | 184 |
| 0 | 6 | 505 | -525 |
| 0 | 8 | 285 | -131 |
| 2 | 0 | 444 | -467 |
| 4 | 0 | 323 | -320 |
| 6 | 0 | 64 | -72 |
| 8 | 0 | 0 | -54 |
| 10 | 0 | 177 | 208 |
| 12 | 0 | 105 | 106 |
| 14 | 0 | 278 | 266 |
| H 11 L | | | |
| 1 | 0 | 394 | -346 |
| 3 | 0 | 390 | -388 |
| 5 | 0 | 121 | 24 |
| 7 | 0 | 292 | 350 |
| 9 | 0 | 107 | -101 |
| 11 | 0 | 161 | -142 |
| 13 | 0 | 115 | 119 |
| H 12 L | | | |
| 0 | 0 | 450 | 481 |
| 0 | 3 | 346 | 314 |
| 2 | 0 | 36 | -12 |
| 4 | 0 | 188 | 164 |
| 6 | 0 | 43 | 37 |
| 8 | 0 | 292 | -376 |
| 10 | 0 | 70 | -91 |
| 12 | 0 | 333 | -343 |
| H 13 L | | | |
| 1 | 0 | 73 | -23 |
| 3 | 0 | 112 | 143 |
| 5 | 0 | 83 | -118 |
| 7 | 0 | 196 | 180 |
| 9 | 0 | 238 | 272 |
| H 14 L | | | |
| 0 | 0 | 61 | -62 |
| 2 | 0 | 351 | -322 |
| 4 | 0 | 58 | -50 |
| 6 | 0 | 90 | 88 |
| 8 | 0 | 0 | -64 |
| H 15 L | | | |
| 1 | 0 | 69 | 80 |
| 3 | 0 | 208 | 224 |

Since this $R$ value looked rather high, it was considered worth while to try the alternative space groups $C2$ and $Cm$. Full-matrix least-squares refinements were therefore carried out in the latter two space groups with the above weighting scheme, and the results are given in Table 1. It appears from the Table that at the significance level of 0·5%, the space group $C2/m$ should be rejected in favour of both $C2$ and $Cm$! Since both the latter space groups could not be simultaneously correct, a careful analysis of the positional and thermal parameters obtained for the three space groups was carried out and the following points were noted:

(i) One of the sulphate oxygen atoms O(2) had a conspicuously high temperature factor of 5·85 Å$^2$ in the space group $C2/m$. (Also in all the three principal projections of nuclear scattering density, the peaks corresponding to O(2) were low in height and highly distorted; see *e.g.* Fig. 1).

(ii) When an atom A in a general position in the space group $C2/m$ was split into two in the space group $C2$, the pair – $A_1$ and (the mirror image of) $A_2$ – moved away almost equally on either side of A. The 'pair-splitting' was generally small except for the atom O(2), being 0·21, 0·37 and 0·44 Å for the three coordinates of the latter. A similar effect was found in the space group $Cm$.

(iii) Atoms on the mirror plane in the space group $C2/m$ moved out of it in $C2$ only by small amounts, ranging from 0·004 to 0·186 Å – the latter value being for O(6).

Now, both O(2) and O(6) belong to the sulphate group containing S(2); in the space group $C2/m$, S(2), O(5) and O(6) are on the mirror plane which also relates the other two oxygen atoms O(2). It was therefore suspected at this stage that this sulphate group was disordered. Hence, in the space group $C2/m$, the atom O(2) was first split into two half-atoms, O(2) and O(2)*, and least-squares refinement continued with isotropic temperature factors. The $R$ value fell quickly to 0·143 and when (in view of point (iii) above) the atom O(6) was also split into two half-atoms by moving it out of the mirror plane, $R$ fell further to 0·135. This $R$ value for $C2/m$ (disordered) corresponding to only 68 variable parameters is superior to the best $R$ value for either $C2$ or $Cm$ with more than 100 variable parameters. The disorder involves the addition of only 5 parameters to $C2/m$ (ordered); from Table 1 it can be confidently asserted that the postulated disorder* is highly significant (Hamilton, 1964, 1965).

However, refinement of the data with anisotropic temperature factors was continued for all the four structures and the results are given in Table 2. This Table

Table 6. *Interatomic distances and bond angles*

The standard deviations are given in parentheses and do not include cell-parameter errors.

(*a*) The Mn octahedra

| | | | |
|---|---|---|---|
| 2 × Mn(1)–O(3) | 2·109 (6) Å | 4 × Mn(2)–$O_w$(1) | 2·193 (5) Å |
| 2 × Mn(1)–$O_w$(2) | 2·188 (8) | 2 × Mn(2)–O(5) | 2·195 |
| 2 × Mn(1)–$O_w$(3) | 2·227 (8) | | |

(*b*) The $SO_1$ groups

| | | | |
|---|---|---|---|
| 1 × S(1)–O(4) | 1·420 (13) Å | 1 × S(2)–O(5) | 1·455 (14) Å |
| 1 × S(1)–O(3) | 1·472 (12) | 1 × S(2)–O(6) | 1·459 (16) |
| 2 × S(1)–O(1) | 1·490 (8) | 1 × S(2)–O(2) | 1·475 (19) |
| | | 1 × S(2)–O(2)* | 1·530 (17) |

(*c*) The water molecules and the hydrogen bonds

| | | | |
|---|---|---|---|
| $O_w$(1)——H(1) | 0·964† (12) Å | H(1)——$O_w$(1)——H(2) | 104·4 (0·6)° |
| | 0·991‡ (13) | O(2)*---$O_w$(1)---O(1) | 97·2 (0·4) |
| $O_w$(1)——H(2) | 0·978† (9) | O(2)----$O_w$(1)---O(1) | 92·7 (0·4) |
| | 0·995‡ (10) | $O_w$(1)——H(1)----O(2)* | 165·7 (1·1) |
| $O_w$(1)---O(2)* | 2·635 (17) | $O_w$(1)——H(1)----O(2) | 165·5 (1·0) |
| $O_w$(1)---O(2) | 2·711 (16) | $O_w$(1)——H(2)----O(1) | 168·1 (0·9) |
| $O_w$(1)---O(1) | 2·697 (6) | | |
| 2 × $O_w$(2)——H(3) | 0·994† (11) Å | H(3)——$O_w$(2)——H(3) | 106·5 (1·5)° |
| | 0·994‡ (13) | O(1)----$O_w$(2)---O(1) | 116·8 (0·4) |
| 2 × $O_w$(2)---O(1) | 2·704 (6) | $O_w$(2)——H(3)----O(1) | 171·4 (1·1) |
| $O_w$(3)——H(4) | 0·942† (23) | H(4)——$O_w$(3)——H(5) | 108·8 (1·8) |
| | 0·970‡ (25) | O(2)----$O_w$(3)---O(6) | 103·8 (0·4) |
| | | | 100·6 (0·4) |
| $O_w$(3)——H(5) | 0·908† (18) | $O_w$(3)——H(4)----O(2) | 147·5 (0·9) |
| | 0·931‡ (20) | $O_w$(3)——H(5)----O(6) | 171·4 (1·0) |
| $O_w$(3)---O(2) | 2·738 (18) | | |
| $O_w$(3)---O(6) | 2·767 (12) | | |

† Uncorrected for thermal motion.

‡ Corrected for thermal motion, assuming that the hydrogen atom 'rides' on the water oxygen atom (Busing & Levy, 1964). This correction is somewhat uncertain since there might be some small residual disorder in parts of the structure other than the sulphate group and this would affect the anisotropic thermal parameters of the atoms. This point is perhaps valid in particular for $O_w$(2)–H(3) (See Table 4).

shows that while $C2/m$ (ordered) can be rejected in favour of $C2/m$ (disordered) at a significance level lower than 0·5%, the latter cannot be rejected in favour of either $C2$ or $Cm$ even at a significance level of 25%.† Further, an examination revealed some poor bond-length and bond-angle values for both $C2$ and $Cm$, as shown in Table 3. Therefore, it was concluded that the space group $C2/m$ represents the true symmetry of the structure, which contains a disordered sulphate group.‡ The complete list of positional and thermal parameters is given in Table 4. The stretched-out contours enveloping O(2) and O(2)* in the projection of nuclear scattering density along the $c$ axis (Fig. 1) vividly illustrate the disorder of the sulphate group. [It is worth noting that in the X-ray Fourier maps given in Figs. 1 and 3 of Schneider's paper as well as in the other projections of nuclear scattering density calculated by us, the peaks for O(2) are much more diffuse and distorted than for, say, O(1)]. The observed and calculated structure factors are compared in Table 5 and the bond lengths and bond angles, calculated using the program *ORFFE* (Busing, Martin & Levy, 1964), are given in Table 6.

## Discussion

A schematic projection of the structure along [010] is shown in Fig. 2. The heavy-atom positions are in generally good agreement with those in Schneider's (1961) structure, except for the disordered sulphate oxygen atoms. The two manganese ions are octahedrally coordinated by sulphate and water oxygen atoms and the Mn–O distances are in agreement with those found in $Mn(NH_4)_2(SO_4)_2.6H_2O$ (Montgomery, Chastain & Lingafelter, 1966) and $MnCl_2.4H_2O$ (Zalkin, Forrester & Templeton, 1964). The potassium ion has nine neighbours at distances ranging from 2·63 to 3·26 Å, the average being 2·96 Å. The (weighted) mean S–O distance of 1·478 Å in this structure compares well with the value of 1·473 Å given by Baur (1964) after examination of a large number of sulphate structures.

All the three non-equivalent water molecules are involved in normal O–H---O hydrogen bonds. It is interesting to note that in $C2/m$ (ordered), the hydrogen H(4) attached to $O_w(3)$ would be perforce involved in a bifurcated hydrogen-bond interaction of the type

$$O_w(3){-}H(4)\begin{matrix} \diagup\, O(2) \\ \\ \diagdown\, O(2) \end{matrix}$$

, the two $O_w$---O(2) distances being 3·04 Å and the two $O_w(3)$–H(4)---O(2) angles 145·2°. But the disordering of the sulphate groups has reduced one of the distances $O_w(3)$---O(2) to 2·74 Å while $O_w(3)$---O(2)* has increased to 3·38 Å, thus eliminating the possibility of a bifurcated hydrogen bond. However, this disordering leads to two alternative hydrogen bonds involving H(1), *viz.* $O_w(1)$–H(1)---O(2) and $O_w(1)$–H(1)---O(2)*, both of which are seen to be satisfactory from Table 6.

The coordination of the three water molecules is shown in Fig. 3. $H_2O_w(3)$ has a trigonal coordination; the bisector of its lone pair orbitals is directed toward the manganese ion Mn(1) and, therefore, it belongs to Type D of our classification (Chidambaram, Sequeira & Sikka, 1964). $H_2O_w(1)$ has a tetrahedral coordination; one of its lone pair orbitals is directed toward the potassium ion and the other toward the manganese ion Mn(2). The bisector of the lone pair orbitals of $H_2O_w(2)$ is directed toward the manganese ion Mn(1); but $O_w(2)$ has, in addition, two potassium neighbours at 3·09 Å nearly normal to the plane of the molecule leading to an approximately trigonal bipyramidal coordination for $H_2O_w(2)$. Somewhat similar coordinations, though with different types of neighbours, have been observed recently in sodium perxenate octahydrate (Ibers, Hamilton & Mackenzie, 1964). The coordination types of $H_2O_w(1)$ and $H_2O_w(2)$ are relatively rare and no examples of these were known to us at the time of our classification referred to above.

While we have introduced disordering in only two of the sulphate oxygen atoms, it is inconceivable that this disorder is not propagated to other atoms in the structure to a small extent. For example, S(2) might be slightly off the mirror plane but attempts to move S(2) from the mirror plane led to a negative temperature factor for it and hence were dropped. Similarly, an inspection of the thermal parameters in Table 4 indicates that $O_w(2)$ is probably a little off the twofold axis and that the atoms O(3) and O(4), as well as the

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† For a discussion regarding a choice between $C2/m$, $C2$ and $Cm$ for the structure of thortveitite (Cruickshank, Lynton & Barclay, 1962), see Hamilton (1965).

‡ The disorder seems to correspond very roughly to a rotation of the sulphate group by about 20° around the S(2)O(5) line – O(2) going into O(2)* and *vice versa* and O(6) going into its mirror image. Recently, Cromer, Kay & Larson (1967) have interpreted the large anisotropic thermal motion of sulphate oxygen atoms observed in $NaAl(SO_4)_2.12H_2O$ in terms of coupled translational and rotational oscillations. A similar interpretation of the present results on $K_2Mn(SO_4)_2.4H_2O$ (in lieu of the disorder) seems to be ruled out by the significance tests described above.

* It was suggested by the referee that it might be worth while to consider a model in the space group $C2$ in which the sulphate group which appears to be disordered in the space group $C2/m$ is 'frozen' into one of the two possible orientations while the other atoms are allowed to be in the positions corresponding to the holosymmetric space group (of course, such a model is not rigorously valid because the sulphate group alone cannot have a symmetry lower than the symmetry of the crystalline field surrounding it; however, one can conceive of small shifts of the other atoms enough to destroy the mirror symmetry and to make one of the sulphate orientations energetically more favoured). Isotropic least-squares refinement of 16 parameters in this way in the space group $C2$ – 4 scale factors and the positional parameters and isotropic temperature factors of O(2), O(2)* and O(6) – reduced the $R$ value to 0·1482, starting from 0·1492. A comparison with the $R$ indices given in Table 1 clearly shows that this 'hybrid' model can be rejected. It may be mentioned that the few parameters refined here converged close to the values found in our earlier more complete refinement in the space group $C2$ referred to in the text.

water molecule H(4)$O_w$(3)H(5) are a little off the mirror plane. But it does not seem possible to isolate these displacements from the thermal parameters in a significant manner. It may also be mentioned that some of the strongest reflexions are affected by secondary extinction; but omission of twelve of the former from the least-squares refinement did not lead to any significant improvement in the thermal parameters like $B_{22}$ of Mn(1). It is probably the small unallowed residual disorder in the structure discussed above that accounts for the unsatisfactory thermal parameters.

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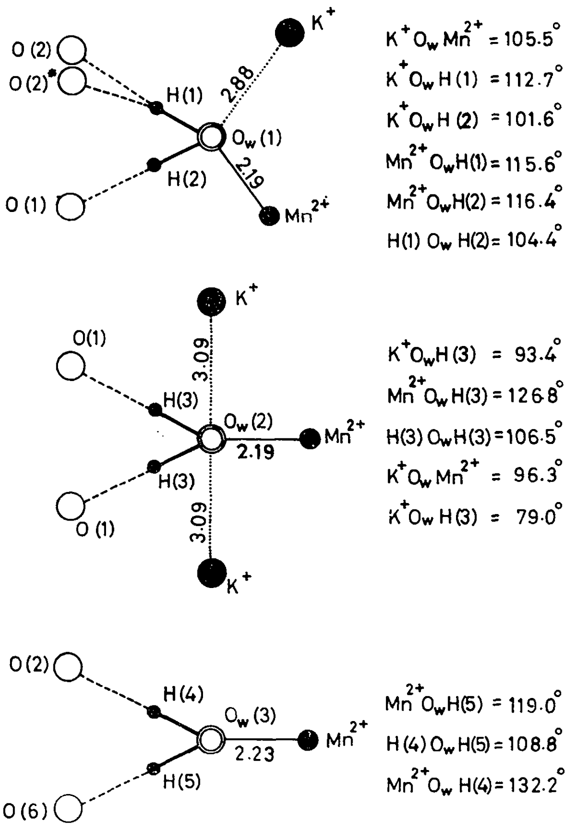

Fig. 3. Coordination of the water molecules in the structure. Note that H(1) is *not* participating in a bifurcated hydrogen bond but is bonded at any instant to *either* (O2) *or* O(2)* only.