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# The Crystal Structure of $Na_2Mg_2Si_6O_{15}$

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The compound $Na_2Mg_2Si_6O_{15}$ is essentially isostructural with tuhualite, $[(Na, K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30}.H_2O]$. The silicate anions are corrugated ribbons, two tetrahedra wide, and are made up from rings of four tetrahedra fused together. Some of the $Mg^{2+}$ ions are tetrahedrally coordinated, and the structure could alternatively be described as being based on a framework with some of the tetrahedral sites occupied by $Mg^{2+}$ and a 7:15 ratio of tetrahedral cations to oxygen. The remaining $Mg^{2+}$ ions are octahedrally coordinated, and of the $Na^+$ ions, some have 9 and others 10 oxygen neighbours within 3·1 Å.

## Introduction

The compound $Na_2Mg_2Si_6O_{15}$ was first described by Botvinkin, Popova & Manuilova (1937), and crystal data for it were reported by Shahid & Glasser (1972). Cradwick, Shahid & Taylor (1972) published a note on the crystal structure, describing the silicate anion, which they found to be a corrugated ribbon, two tetrahedra wide. This was wrongly described as a new type of silicate anion; Dr S. Merlino has since drawn our attention to the fact that the same anion occurs in the mineral tuhualite, $[(Na,K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30}.H_2O]$, the structure of which he had determined earlier (Merlino, 1969), and comparison of the two structures shows them to be essentially isostructural. In this paper we report the structure of $Na_2Mg_2Si_6O_{15}$, of which only some features were described in the previous note.

## Crystal data

The crystal data, found by Shahid & Glasser (1972) and confirmed by us by powder diffractometry ($\lambda$ for Cu $K\alpha = 1{\cdot}5418$ Å), were as follows: orthorhombic, *Cmca* or *C2cb*, $a = 14{\cdot}165$, $b = 17{\cdot}59$, $c = 10{\cdot}205$ Å, $V = 2542{\cdot}7$ Å$^3$, $Z = 8$, $D_x = 2{\cdot}629$ g.cm$^{-3}$. Our own results show the space group to be *Cmca*. The *a* and *c* axes are here interchanged relative to those used in the earlier reports, to make them the same as those used by Merlino (1969).

## Experimental methods, structure determination and refinement

Preparation of single-crystal material is difficult as the compound, which melts incongruently, has so far been obtained only by cooling melts that are both highly viscous and of different composition from itself; Dr F. P. Glasser and Dr K. A. Shahid kindly provided a specimen. It was an irregular fragment, a few tenths of a millimetre in its longest dimension, and consisted of the crystal embedded in a larger amount of glass, from which it could not be separated. Intensity data were collected using an automatic linear diffractometer with Mo $K\alpha$ radiation, except for a few reflexions for which this gave uncertain results, and for which intensities were estimated visually from Weissenberg photographs. In general, the intensities of four equivalent reflexions were averaged to give that of each independent reflexion. Data were recorded for 630 independent reflexions, of which 390 were observed. No absorption corrections were applied.

Computing was largely done using programs kindly supplied by Dr F. R. Ahmed and collaborators, of the National Research Council of Canada, and adapted by Mr J. S. Knowles of the Department of Computing, University of Aberdeen. Form factors (for $Na^+$, $Mg^{2+}$, Si and $O^-$) were taken from *International Tables for X-ray Crystallography* (1962).

$E$ values were calculated for the reflexions, and their distribution showed that a centre of symmetry was present, indicating the space group *Cmca*. The structure was solved by symbolic addition, which yielded four possible solutions, for each of which an $E$ map was calculated. The most promising of these gave chemically reasonable coordinates for all the atoms except one sodium. A structure-factor calculation gave an initial $R$ value of 0·43 on the 630 independent reflexions. One cycle of Fourier refinement gave the position of the remaining sodium atom and slightly altered coordinates for the other atoms; the parameters were then refined by block-diagonal least squares, first the coordinates only, then also the scale factor and individual isotropic temperature factors. Only the observed reflexions were used in the refinement; in the course of the latter some wrong intensities were corrected, and it was decided to restrict the reflexions used to those contained in a cylinder of reciprocal space, with its axis parallel to $\mathbf{a}^*$, of radius 0·86 Å$^{-1}$ and extending to 0·76 Å$^{-1}$ along $\mathbf{a}^*$. This cylinder contained 468 independent reflexions, of which 358 were observed, and was chosen to reduce the large number of unobserved reflexions while losing the minimum number of observed ones. The refinement converged at $R=0\cdot082$ on the observed reflexions, or $R=0\cdot121$ if the unobserved ones were also included. The weighting scheme used in the later stages of refinement was $w=1/\{1+[(|F_{\rm obs}|-105\cdot0)/25\cdot0]^2\}$ and analyses against $|F_{\rm obs}|$, $\sin^2\theta$, and $h$ index showed it to be reasonably satisfactory. A final, difference electron-density map was calculated; the extreme values on it were $+0\cdot7$ and $-0\cdot6$ e.Å$^{-3}$. Tables 1 to 3 give respectively the final parameters, the observed and calculated structure factors, and the more important interatomic distances and angles.

Table 1. *Atomic parameters*

Fractional coordinates are multiplied by $10^4$.

| | Equi-point | $x/a$ | $y/b$ | $z/c$ | $B_{\rm iso}$ (Å$^2$) |
|---|---|---|---|---|---|
| Si(1) | 16(*g*) | 3889 (4) | 1326 (3) | 151 (5) | 1·0 (1) |
| Si(2) | 16(*g*) | 3877 (4) | 751 (3) | 3098 (5) | 1·1 (1) |
| Si(3) | 16(*g*) | 3862 (4) | 1924 (3) | 5389 (5) | 1·1 (1) |
| Mg(1) | 8(*d*) | 2490 (8) | 0 | 0 | 0·8 (2) |
| Mg(2) | 8(*e*) | 2500 | −899 (5) | 2500 | 1·2 (2) |
| Na(1) | 8(*f*) | 0 | 4099 (7) | 2568 (14) | 3·4 (3) |
| Na(2) | 8(*e*) | 2500 | 2313 (6) | 2500 | 1·8 (2) |
| O(1) | 16(*g*) | 3611 (9) | 2227 (6) | −18 (11) | 0·9 (2) |
| O(2) | 16(*g*) | 3268 (8) | 783 (7) | −790 (11) | 0·8 (3) |
| O(3) | 16(*g*) | 3681 (10) | 1105 (7) | 1684 (13) | 1·8 (3) |
| O(4) | 16(*g*) | 3327 (9) | 13 (7) | 3414 (12) | 1·2 (3) |
| O(5) | 16(*g*) | 3577 (10) | 1424 (6) | 4125 (11) | 1·3 (3) |
| O(6) | 16(*g*) | 3393 (10) | 1671 (8) | 6702 (11) | 1·7 (3) |
| O(7) | 8(*f*) | 5000 | 1223 (11) | −164 (18) | 2·2 (4) |
| O(8) | 8(*f*) | 5000 | 546 (12) | 3215 (19) | 2·8 (5) |
| O(9) | 8(*f*) | 5000 | 1830 (12) | 5575 (21) | 2·7 (4) |

Table 2. *Observed and calculated structure factors* ( × 10)

Unobserved reflexions marked *.

| L | FO | FC |
|---|---|---|
| H= 0, K= 0 | | |
| 2 | 1892 | 2069 |
| 4 | 3468 | 3901 |
| 6 | 2596 | 2486 |
| 8 | 585 | 162 |
| H= 0, K= 2 | | |
| 0 | 186 | 338 |
| 2 | 2720 | -3080 |
| 3 | 206* | 158 |
| 4 | 1463 | -1553 |
| 5 | 2260 | 2149 |
| 6 | 763 | 752 |
| 7 | 1184 | -1103 |
| 8 | 343* | -457 |
| H= 0, K= 4 | | |
| 0 | 3041 | -3356 |
| 1 | 1587 | -1758 |
| 2 | 389 | -167 |
| 3 | 647 | -591 |
| 4 | 249* | -12 |
| 5 | 1362 | 1366 |
| 6 | 299* | 313 |
| 7 | 3483 | -3615 |
| H= 0, K= 6 | | |
| 0 | 751 | -590 |
| 1 | 332 | 105 |
| 2 | 3299 | 3604 |
| 3 | 2739 | 2924 |
| 4 | 1070 | -1054 |
| 5 | 1074 | 1078 |
| 6 | 1729 | 1721 |
| 7 | 1428 | 1420 |
| H= 0, K= 8 | | |
| 0 | 524 | 343 |
| 1 | 351 | 226 |
| 2 | 1295 | 1352 |
| 3 | 1009 | -1066 |
| 4 | 964 | 865 |
| 5 | 2045 | -2023 |
| 6 | 1382 | 1343 |
| H= 0, K= 10 | | |
| 0 | 2185 | 2123 |
| 1 | 1433 | -1374 |
| 2 | 500 | 249 |
| 3 | 1072 | -1059 |
| 4 | 1147 | 1046 |
| 5 | 1867 | -1817 |
| H= 0, K= 12 | | |
| 0 | 1527 | 1455 |
| 1 | 1767 | 1674 |
| 2 | 2607 | -2577 |
| 3 | 330* | 200 |
| 4 | 734 | -609 |
| H= 0, K= 14 | | |
| 0 | 2371 | 2340 |
| H= 1, K= 1 | | |
| 1 | 257 | 79 |
| 2 | 597 | 677 |
| 3 | 2731 | -2730 |
| 4 | 752 | 792 |
| 5 | 453 | 359 |
| 6 | 1097 | 1043 |
| 7 | 1101 | -983 |
| 8 | 1441 | 1440 |
| H= 1, K= 3 | | |
| 1 | 349 | -14 |
| 2 | 1566 | -1697 |
| 3 | 214* | -78 |
| 4 | 242* | -37 |
| 5 | 1583 | 1563 |
| 6 | 1030 | -937 |
| 7 | 1414 | 1371 |
| H= 1, K= 5 | | |
| 1 | 2682 | 2684 |
| 2 | 1571 | -1617 |
| 3 | 1120 | 1086 |
| 4 | 1084 | 1004 |
| 5 | 282* | 117 |
| 6 | 1315 | -1262 |
| 7 | 592 | 546 |
| H= 1, K= 7 | | |
| 1 | 940 | -873 |
| 2 | 551 | 458 |
| 3 | 466 | -388 |
| 4 | 1220 | 1148 |
| 5 | 2181 | -2055 |
| 6 | 880 | 727 |
| H= 1, K= 9 | | |
| 1 | 1807 | -1824 |
| 2 | 277* | -73 |
| 3 | 288* | -55 |
| 4 | 1459 | -1339 |
| 5 | 1449 | -1432 |
| H= 1, K= 11 | | |
| 1 | 2066 | 2028 |
| 2 | 1313 | 1235 |
| 3 | 1239 | 1238 |
| 4 | 509 | -149 |
| 5 | 1870 | 1803 |
| H= 1, K= 13 | | |
| 2 | 619 | 570 |
| 3 | 1797 | -1710 |
| H= 2, K= 0 | | |
| 2 | 893 | 862 |
| 4 | 231* | -52 |
| 6 | 288* | 460 |
| 8 | 818 | -933 |
| H= 2, K= 2 | | |
| 0 | 190 | -528 |
| 2 | 2140 | -2120 |
| 3 | 437 | 293 |
| 4 | 366 | 127 |
| 5 | 632 | 577 |
| 6 | 542 | -531 |
| 7 | 317* | -87 |
| H= 2, K= 4 | | |
| 0 | 2190 | -2142 |
| 1 | 1281 | -1226 |
| 2 | 822 | -784 |
| 3 | 525 | -507 |
| 4 | 1640 | -1727 |
| 5 | 983 | -962 |
| 6 | 1036 | -981 |
| 7 | 325* | 44 |
| H= 2, K= 6 | | |
| 0 | 561 | -390 |
| 1 | 219* | -47 |
| 2 | 375 | 69 |
| 3 | 433 | -266 |
| 4 | 460 | 348 |
| 5 | 664 | 653 |
| 6 | 1697 | -1793 |
| 7 | 516 | -256 |
| H= 2, K= 8 | | |
| 0 | 1646 | -1467 |
| 1 | 418 | -382 |
| 2 | 262* | 295 |
| 3 | 589 | 643 |
| 4 | 447 | -367 |
| 5 | 354* | 118 |
| 6 | 530 | -418 |
| H= 2, K= 10 | | |
| 0 | 743 | -703 |
| 1 | 1228 | 1104 |
| 2 | 292* | -231 |
| 3 | 531 | -439 |
| 4 | 316* | -288 |
| H= 2, K= 12 | | |
| 0 | 1692 | -1656 |
| 1 | 316* | -56 |
| 2 | 678 | -562 |
| 3 | 719 | 636 |
| 4 | 524 | -608 |
| H= 2, K= 14 | | |
| 0 | 940 | -823 |
| 2 | 697 | -745 |
| H= 3, K= 1 | | |
| 1 | 123* | -31 |
| 2 | 330 | -228 |
| 3 | 1278 | 1281 |
| 4 | 997 | 974 |
| 5 | 262* | -381 |
| 6 | 576 | -573 |
| 7 | 502 | -173 |
| 8 | 1654 | -1570 |
| H= 3, K= 3 | | |
| 1 | 256 | 136 |
| 2 | 821 | 844 |
| 3 | 422 | -142 |
| 4 | 889 | 779 |
| 5 | 813 | -750 |
| 6 | 460 | 403 |
| H= 3, K= 5 | | |
| 1 | 1247 | -1266 |
| 2 | 879 | 825 |
| 3 | 1519 | 1356 |
| 4 | 749 | -675 |
| 5 | 322* | 26 |
| 6 | 942 | 829 |
| H= 3, K= 7 | | |
| 1 | 1674 | -1595 |
| 2 | 523 | -448 |
| 3 | 665 | 629 |
| 4 | 281* | 162 |
| 5 | 969 | 960 |
| 6 | 507 | -333 |
| 7 | 344* | 13 |
| H= 3, K= 9 | | |
| 1 | 583 | 562 |
| 2 | 463 | -365 |
| 3 | 289* | 30 |
| 4 | 573 | 499 |
| 5 | 931 | 924 |
| H= 3, K= 11 | | |
| 1 | 968 | -956 |
| 2 | 935 | -903 |
| 3 | 317* | -77 |
| 4 | 600 | -526 |
| 5 | 1769 | -1743 |
| H= 3, K= 13 | | |
| 3 | 1888 | 1922 |
| H= 4, K= 0 | | |
| 2 | 3144 | -2989 |
| 4 | 1162 | 1165 |
| 8 | 1930 | 1909 |
| H= 4, K= 2 | | |
| 0 | 1566 | 1704 |
| 1 | 2552 | 2744 |
| 2 | 3144 | 3042 |
| 3 | 646 | -742 |
| 4 | 1763 | 1911 |
| 5 | 575 | 587 |
| 6 | 831 | 887 |
| 7 | 319* | 96 |
| 8 | 1079 | 1044 |
| H= 4, K= 4 | | |
| 0 | 2649 | 2617 |
| 1 | 2584 | 2750 |
| 2 | 705 | 669 |
| 3 | 1653 | -1666 |
| 4 | 251* | 117 |
| 5 | 828 | 887 |
| 6 | 1291 | 1064 |
| 7 | 1234 | 1161 |
| H= 4, K= 6 | | |
| 0 | 869 | -967 |
| 1 | 1835 | -1816 |
| 2 | 1103 | 1071 |
| 3 | 1008 | -978 |
| 4 | 727 | -671 |
| 5 | 1581 | -1611 |
| 6 | 1586 | 1644 |
| 7 | 1041 | -961 |
| H= 4, K= 8 | | |
| 0 | 663 | 535 |
| 1 | 1562 | -1544 |
| 2 | 263* | 18 |
| 3 | 1795 | 1775 |
| 4 | 785 | 836 |
| 5 | 830 | 842 |
| H= 4, K= 10 | | |
| 0 | 450 | 346 |
| 1 | 957 | -979 |
| 2 | 293* | 186 |
| 3 | 2111 | 2078 |
| 4 | 915 | 904 |
| 6 | 634 | -439 |
| H= 4, K= 12 | | |
| 0 | 1232 | 1210 |
| 1 | 317* | 264 |
| 2 | 1616 | 1656 |
| 3 | 1415 | -1309 |
| 4 | 2016 | 2024 |
| H= 4, K= 14 | | |
| 0 | 1245 | -1280 |
| 1 | 627 | 516 |
| H= 5, K= 1 | | |
| 1 | 196 | 65 |
| 2 | 390 | -379 |
| 3 | 203* | 172 |
| 4 | 1360 | -1579 |
| 5 | 434 | 342 |
| 6 | 997 | -915 |
| 7 | 1343 | 1316 |
| 8 | 1274 | -1280 |
| H= 5, K= 3 | | |
| 1 | 164* | -56 |
| 2 | 188* | -47 |
| 3 | 217* | -166 |
| 4 | 1048 | -1070 |
| 5 | 631 | -600 |
| 6 | 804 | 658 |
| 7 | 506 | -431 |
| H= 5, K= 5 | | |
| 1 | 203* | -278 |
| 2 | 335 | 125 |
| 3 | 1621 | -1635 |
| 4 | 261* | -313 |
| 5 | 285* | -221 |
| 6 | 1115 | 1115 |
| 7 | 567 | -501 |
| 8 | 754 | 710 |
| H= 5, K= 7 | | |
| 1 | 2015 | 2092 |
| 2 | 287* | 108 |
| 3 | 264* | -68 |
| 4 | 283* | -130 |
| 5 | 1476 | 1486 |
| 6 | 324* | -455 |
| H= 5, K= 9 | | |
| 1 | 783 | 779 |
| 2 | 468 | -146 |
| 3 | 292* | -171 |
| 4 | 1565 | 1520 |
| 5 | 710 | 679 |
| H= 5, K= 11 | | |
| 1 | 1613 | -1618 |
| 2 | 1031 | -996 |
| 3 | 1128 | -1197 |
| 4 | 553 | 511 |
| 5 | 1288 | -1243 |
| H= 5, K= 13 | | |
| 3 | 1281 | 1308 |
| H= 6, K= 0 | | |
| 2 | 164* | -48 |
| 4 | 2458 | -2718 |
| 6 | 292* | -33 |
| 8 | 1069 | -1140 |
| H= 6, K= 2 | | |
| 0 | 125* | 457 |
| 1 | 708 | 898 |
| 2 | 950 | -1075 |
| 3 | 403 | 213 |
| 4 | 744 | -653 |
| 5 | 268* | 100 |
| 6 | 750 | -839 |
| 7 | 864 | 747 |
| H= 6, K= 4 | | |
| 0 | 724 | -777 |
| 1 | 341 | -282 |
| 2 | 336 | -228 |
| 3 | 1042 | 991 |
| 4 | 422 | -302 |
| 5 | 492 | 541 |
| 6 | 762 | 856 |
| H= 6, K= 6 | | |
| 0 | 810 | 702 |
| 1 | 509 | 485 |
| 2 | 2371 | -2575 |
| 3 | 287* | -357 |
| 4 | 833 | -827 |
| 5 | 295* | -132 |
| 6 | 318* | -46 |
| 7 | 906 | -897 |
| H= 6, K= 8 | | |
| 0 | 254* | -366 |
| 1 | 449 | -427 |
| 2 | 771 | -728 |
| 3 | 279* | -139 |
| 4 | 808 | -830 |
| 5 | 315* | -331 |
| H= 6, K= 10 | | |
| 0 | 541 | -619 |
| 1 | 598 | -614 |
| 2 | 489 | -526 |
| 3 | 557 | -573 |
| 4 | 486 | -453 |
| 5 | 875 | 817 |
| H= 6, K= 12 | | |
| 0 | 318* | 288 |
| 1 | 556 | -622 |
| 2 | 326* | 249 |
| 3 | 335* | 322 |
| 4 | 868 | -777 |
| H= 6, K= 14 | | |
| 1 | 693 | 639 |
| H= 7, K= 1 | | |
| 1 | 210 | 277 |
| 2 | 168* | 291 |
| 4 | 371 | -350 |
| 5 | 267* | -133 |
| 6 | 451 | 387 |
| 7 | 583 | -467 |
| 8 | 723 | 688 |
| H= 7, K= 3 | | |
| 1 | 273 | -247 |
| 2 | 636 | -470 |
| 3 | 219* | 22 |
| 4 | 454 | -457 |
| 5 | 837 | 897 |
| 6 | 567 | -295 |
| 7 | 825 | 811 |
| H= 7, K= 5 | | |
| 1 | 797 | 757 |
| 2 | 460 | -447 |
| 3 | 241* | -427 |
| 4 | 766 | 855 |
| 5 | 288* | 36 |
| 6 | 508 | -417 |
| H= 7, K= 7 | | |
| 1 | 529 | 507 |
| 2 | 252* | 107 |
| 3 | 267* | 32 |
| 4 | 783 | 661 |
| 5 | 701 | -570 |
| 6 | 587 | 317 |
| H= 7, K= 9 | | |
| 1 | 1181 | -1261 |
| 2 | 476 | -451 |
| 3 | 295* | -61 |
| 4 | 695 | -659 |
| 5 | 990 | -890 |
| H= 7, K= 11 | | |
| 1 | 736 | 740 |
| 2 | 621 | 517 |
| 3 | 622 | 562 |
| 4 | 335* | -9 |
| 5 | 1003 | 929 |
| H= 7, K= 13 | | |
| 1 | 338* | -77 |
| 2 | 681 | 602 |
| 3 | 961 | -983 |
| H= 8, K= 0 | | |
| 2 | 586 | 840 |
| 6 | 1149 | 1253 |
| H= 8, K= 2 | | |
| 0 | 451 | -707 |
| 1 | 782 | -880 |
| 2 | 1164 | -1337 |
| 3 | 212* | -590 |
| 4 | 243* | -144 |
| 5 | 1127 | 1321 |
| 6 | 620 | 611 |
| 7 | 854 | -869 |
| H= 8, K= 4 | | |
| 0 | 1134 | -1465 |
| 1 | 673 | -602 |
| 2 | 421 | 470 |
| 3 | 1310 | -1416 |
| 4 | 257* | 135 |
| 5 | 282* | 29 |
| 6 | 545 | -402 |
| 7 | 1981 | -1886 |
| H= 8, K= 6 | | |
| 0 | 827 | -885 |
| 1 | 226* | -172 |
| 2 | 3331 | 3431 |
| 3 | 1528 | 1498 |
| 4 | 276* | -195 |
| 5 | 616 | 549 |
| 6 | 322* | -113 |
| 7 | 923 | 1027 |
| H= 8, K= 8 | | |
| 0 | 257* | 248 |
| 1 | 260* | 57 |
| 2 | 1159 | 1219 |
| 3 | 283* | 45 |
| 4 | 722 | 690 |
| 5 | 933 | -779 |
| H= 8, K= 10 | | |
| 0 | 942 | 1041 |
| 1 | 293* | -133 |
| 2 | 300* | 324 |
| 3 | 311* | 22 |
| 4 | 1020 | 1020 |
| 5 | 1205 | -1133 |
| H= 8, K= 12 | | |
| 0 | 322* | -322 |
| 1 | 1206 | 1196 |
| 2 | 1550 | -1500 |
| 4 | 520 | 298 |
| H= 8, K= 14 | | |
| 1 | 355* | -14 |
| H= 9, K= 1 | | |
| 1 | 127* | -94 |
| 2 | 171* | 389 |
| 3 | 208* | -718 |
| 4 | 2047 | 2125 |
| 5 | 271* | -86 |
| 6 | 772 | 911 |
| 7 | 1467 | -1511 |
| 8 | 871 | 769 |
| H= 9, K= 3 | | |
| 1 | 168* | 155 |
| 2 | 458 | -442 |
| 3 | 222* | -65 |
| 4 | 1036 | 1099 |
| 5 | 730 | 784 |
| 6 | 671 | -810 |
| 7 | 653 | 546 |
| H= 9, K= 5 | | |
| 1 | 866 | 1022 |
| 2 | 589 | -532 |
| 3 | 2604 | 2629 |
| 4 | 268* | 202 |
| 5 | 292* | 230 |
| 6 | 1017 | -1023 |
| H= 9, K= 7 | | |
| 1 | 2563 | -2795 |
| 2 | 292* | -42 |
| 3 | 271* | 187 |
| 4 | 931 | 858 |
| 5 | 1845 | -1694 |
| 6 | 681 | 574 |
| H= 9, K= 9 | | |
| 1 | 1030 | -1025 |
| 2 | 287* | -20 |
| 3 | 299* | 121 |
| 4 | 1531 | -1492 |
| 5 | 617 | -674 |
| H= 9, K= 11 | | |
| 1 | 1720 | 1756 |
| 2 | 1004 | 934 |
| 3 | 1658 | 1551 |
| 4 | 837 | -776 |
| 5 | 881 | 847 |
| 6 | 795 | 996 |
| H= 9, K= 13 | | |
| 3 | 712 | -681 |
| H= 10, K= 0 | | |
| 2 | 894 | 900 |
| 4 | 241* | 514 |
| 6 | 728 | 758 |
| 8 | 892 | -947 |
| H= 10, K= 2 | | |
| 0 | 128* | 43 |
| 1 | 507 | -538 |
| 2 | 1260 | -1382 |
| 3 | 715 | 890 |
| 4 | 247* | -180 |
| 5 | 276* | 483 |
| 6 | 304* | -133 |
| 7 | 331* | -502 |
| H= 10, K= 4 | | |
| 0 | 1844 | -1601 |
| 1 | 1094 | -1094 |
| 2 | 1107 | -1153 |
| 3 | 265* | -118 |
| 4 | 1646 | -1763 |
| 5 | 910 | -846 |
| 6 | 1234 | -1307 |
| 7 | 551 | -490 |
| H= 10, K= 6 | | |
| 0 | 225* | -491 |
| 1 | 229* | -173 |
| 2 | 596 | 557 |
| 3 | 379 | 166 |
| 4 | 737 | 728 |
| 5 | 1035 | 1005 |
| 6 | 910 | -950 |
| H= 10, K= 8 | | |
| 0 | 1555 | -1471 |
| 1 | 264 | 54 |
| 2 | 274* | 300 |
| 3 | 287* | 50 |
| 4 | 304* | 13 |
| 5 | 324* | -26 |
| H= 10, K= 10 | | |
| 0 | 295* | -169 |
| 1 | 917 | 1120 |
| 2 | 305* | 38 |
| 3 | 869 | -802 |
| 4 | 537 | -406 |
| 5 | 553 | -488 |
| H= 10, K= 12 | | |
| 0 | 943 | -1021 |
| 1 | 370* | 223 |
| 2 | 824 | -917 |
| 3 | 539 | 389 |
| 4 | 805 | -822 |

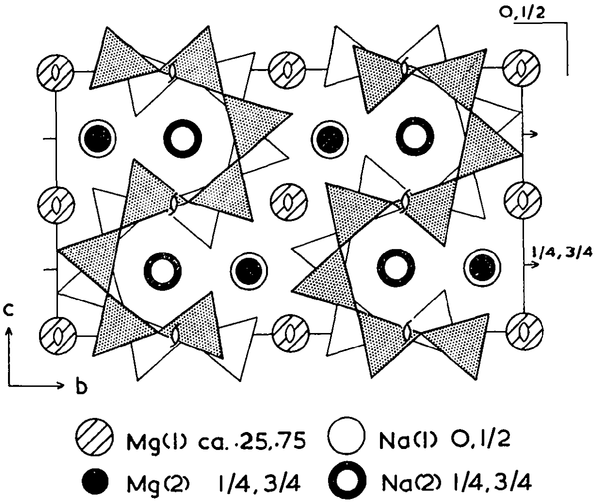

Fig. 1. Unit cell of $Na_2Mg_2Si_6O_{15}$ projected along **a**.

## Description of the structure

Fig. 1 shows the structure projected along **a**, and Fig. 2 shows selected parts of it to indicate the coordination of the Na, Mg and Si atoms. The silicate anions are corrugated ribbons running parallel to **c**; there are two such ribbons to the height of the cell in the **a** direction, which are shown in Fig. 1 as chains of open and shaded triangles respectively. Each ribbon is two tetrahedra wide in the **a** direction, and repeats at intervals of six such pairs of tetrahedra. The ribbon can also be described as a series of rings of four tetrahedra which are fused together and which lie in planes parallel to [100]. Each triangle in Fig. 1 represents an $Si_2O_7$ group with its Si–Si direction normal to the plane of the paper, the two tetrahedra in the group coinciding in projection because the oxygen atoms that link them lie on planes of symmetry perpendicular to **a**. The Si–O bond lengths (Table 3) are 1·55–1·64 Å; the bonds involving oxygen atoms linked to only one silicon [O(2), O(4) and O(6)] are 1·55–1·62 Å, and those involving oxygen atoms linked to two silicons are 1·59–1·64 Å.

The Mg(1) atoms are tetrahedrally coordinated and, as Merlino (1969) pointed out in relation to tuhualite, the structure can alternatively be described in accordance with Zoltai's (1960) classification as being of a framework type with a ratio of tetrahedral cations to oxygen of 7:15. The Mg(1)–O distances are 1·94 and 1·99 Å. As in tuhualite, this tetrahedron is strongly distorted, with O–Mg–O angles of 90·0–131·4°. The Mg(2) atoms are octahedrally coordinated, with Mg–O distances of 2·03–2·19 Å and relatively slight distortion. The Na(1) atoms have nine oxygen neighbours within 3·1 Å; six of the bonds are directed roughly to the corners of a trigonal prism with its axis parallel to **a**, and the three others to the centres of the prism faces. The first six neighbours are at 2·75–3·06 Å, and the latter three at 2·50–2·63 Å. The Na(2) atoms are irregularly coordinated, with ten neighbours within 3·1 Å. Two of these are much closer (2·34 Å) than the other eight (2·74–3·09 Å).

Table 4 gives the coordination of the oxygen atoms. The sums of the electrostatic valencies received by each oxygen were calculated on the classical assumption that all bonds from each cation are of equal electrostatic bond strength; all Na–O contacts shorter than 3·1 Å were treated as bonds. On these assumptions, the electrostatic valency rule is not well obeyed, O(6) in particular being underbonded and O(1) overbonded. The underbonding of O(6) is compensated by the fact that the bonds from this atom to Na(2) and Si(3) are short, and the overbonding of O(1) is compensated by the fact that its bonds to Si(1) and especially to Na(2) are long. Merlino (1969) noted a similar effect for O(6) in tuhualite. Attempts were made to treat the bonding situation in greater detail by the methods of Donnay & Allmann (1970) and Baur (1971) but they gave inconclusive results.

Table 3. *Interatomic distances* (Å) *and angles* (°)

| | | | | | |
|---|---|---|---|---|---|
| Si(1)–O(1)* | 1·64 (1) | Si(2)–O(3)* | 1·60 (1) | Si(3)–O(1)* | 1·59 (1) |
| Si(1)–O(2) | 1·62 (1) | Si(2)–O(4) | 1·55 (1) | Si(3)–O(5)* | 1·61 (1) |
| Si(1)–O(3)* | 1·64 (1) | Si(2)–O(5)* | 1·64 (1) | Si(3)–O(6) | 1·56 (1) |
| Si(1)–O(7)* | 1·62 (1) | Si(2)–O(8)* | 1·64 (1) | Si(3)–O(9)* | 1·63 (1) |
| Mg(1)–O(2) | 1·94 (1) | Na(1)–O(2) | 3·06 (1) | Na(2)–O(1) | 3·02 (1) |
| Mg(1)–O(4) | 1·99 (1) | Na(1)–O(4) | 2·99 (2) | Na(2)–O(1′) | 3·09 (1) |
| | | Na(1)–O(6) | 2·75 (2) | Na(2)–O(3) | 2·83 (2) |
| Mg(2)–O(2) | 2·07 (1) | Na(1)–O(7) | 2·52 (2) | Na(2)–O(5) | 2·74 (1) |
| Mg(2)–O(4) | 2·19 (1) | Na(1)–O(8) | 2·63 (2) | Na(2)–O(6) | 2·34 (2) |
| Mg(2)–O(6) | 2·03 (1) | Na(1)–O(9) | 2·50 (2) | | |
| Angles at Si(1) | | Angles at Si(2) | | Angles at Si(3) | |
| O(1)–O(2) | 112·2 (7) | O(3)–O(4) | 115·3 (8) | O(1)–O(5) | 104·3 (7) |
| O(1)–O(3) | 106·6 (7) | O(3)–O(5) | 104·6 (7) | O(1)–O(6) | 113·4 (7) |
| O(1)–O(7) | 108·7 (7) | O(3)–O(8) | 108·7 (8) | O(1)–O(9) | 110·3 (8) |
| O(2)–O(3) | 109·3 (7) | O(4)–O(5) | 110·0 (7) | O(5)–O(6) | 115·1 (7) |
| O(2)–O(7) | 110·2 (8) | O(4)–O(8) | 106·8 (8) | O(5)–O(9) | 106·5 (8) |
| O(3)–O(7) | 109·8 (8) | O(5)–O(8) | 111·5 (8) | O(6)–O(9) | 106·9 (8) |

| | |
|---|---|
| Angles at Mg(1) | |
| O(2)–O(2′) | 110·8 (6) |
| O(2)–O(4) | 131·4 (6) |
| O(2)–O(4′) | 90·0 (6) |
| O(4)–O(4′) | 108·9 (6) |
| Angles at Mg(2) | |
| O(2)–O(2′) | 168·7 (5) |
| O(2)–O(4) | 81·4 (5) |
| O(2)–O(4′) | 90·3 (5) |
| O(2)–O(6) | 94·4 (5) |
| O(2)–O(6′) | 93·2 (5) |
| O(4)–O(4′) | 86·1 (5) |
| O(4)–O(6) | 173·7 (6) |
| O(4)–O(6′) | 89·2 (5) |
| O(6)–O(6′) | 95·8 (6) |

* Bridging oxygens. ′ Symmetry-related atoms.

Table 4. *Coordination of the oxygen atoms*

| Oxygen atom | Coordinated atoms | E.s.v. sum |
|---|---|---|
| O(1) | Si(1), Si(3), Na(2), Na(2) | 2·20 |
| O(2) | Si(1), Mg(1), Mg(2), Na(1) | 1·94 |
| O(3) | Si(1), Si(2), Na(2) | 2·10 |
| O(4) | Si(2), Mg(1), Mg(2), Na(1) | 1·94 |
| O(5) | Si(2), Si(3), Na(2) | 2·10 |
| O(6) | Si(3), Mg(2), Na(1), Na(2) | 1·54 |
| O(7) | Si(1), Si(1), Na(1) | 2·11 |
| O(8) | Si(2), Si(2), Na(1) | 2·11 |
| O(9) | Si(3), Si(3), Na(1) | 2·11 |

## Relationships to other structures

The close relationship to tuhualite $[(Na,K)_2Fe_2^{2+}Fe_2^{3+}Si_{12}O_{30}.H_2O]$ has already been noted. In tuhualite, the tetrahedral cation sites are occupied by $Fe^{2+}$ and the octahedral sites by $Fe^{3+}$; the Na(2) sites of the present structure are occupied by $Na^+$ or $K^+$, and the Na(1) sites are empty. The $H_2O$ molecules, which are absent in $Na_2Mg_2Si_6O_{15}$, were considered to be randomly placed in the same channels parallel to the *a* axis as the $Na^+$ and $K^+$ ions.

Merlino (1969) noted that tuhualite was structurally related to osumilite $[(K,Na)(Fe,Mg)_2(Al,Fe)_3(Al,Si)_{12}O_{30}]$, and Shahid & Glasser (1972) and Cradwick, Shahid & Taylor (1972) noted a closely similar relationship of $Na_2Mg_2Si_6O_{15}$ to $Na_2Mg_5Si_{12}O_{30}$, which has an osumilite-type structure. The structure of $Na_2Mg_5Si_{12}O_{30}$ is known most precisely by analogy with that of $K_2Mg_5Si_{12}O_{30}$, which was determined by Khan, Baur & Forbes (1972). Some of the $K^+$ ions in $K_2Mg_5Si_{12}O_{30}$ occupy 9-coordinated sites, which are closely similar in environment and coordination geometry to those occupied by Na(1) in $Na_2Mg_2Si_6O_{15}$; these sites have no counterparts in osumilite or tuhualite. $Na_2Mg_2Si_6O_{15}$ is thus more closely related to $K_2Mg_5Si_{12}O_{30}$ than to osumilite.

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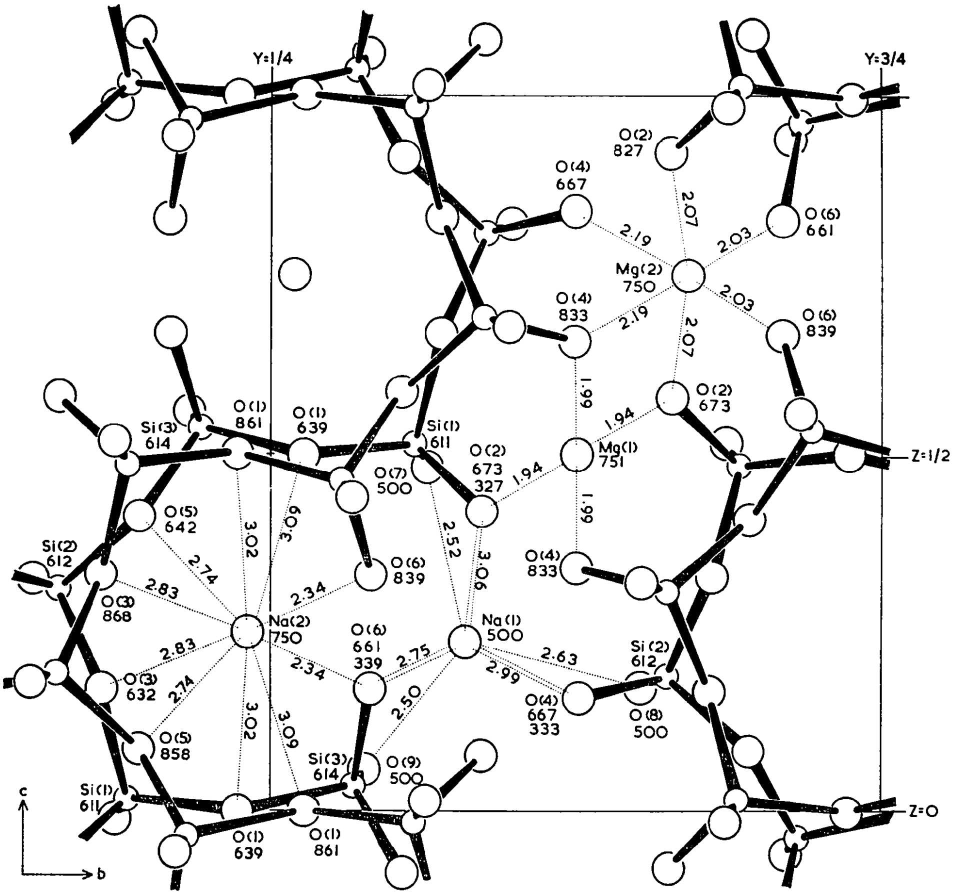

Fig. 2. Selected parts of the structure, projected along **a**, showing the coordination of the Na, Mg and Si atoms. Heights are shown as 1000 *x*/*a*.

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# The Crystal and Molecular Structure of $HK_8Rh_3Br_{18}.10H_2O$

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The crystal and molecular structure of $HK_8Rh_3Br_{18}.10H_2O$ has been determined by three-dimensional X-ray analysis. The crystals are orthorhombic with space group *Pbam* and 2 molecules in the unit cell of dimensions $a=15{\cdot}32$, $b=16{\cdot}63$ and $c=9{\cdot}30$ Å. Two monomeric $RhBr_6$ octahedra exist which are not related by the crystal symmetry.

## Introduction

A series of complexes of formula $K_{3-N}RhBr_{6-N}(H_2O)_N$ ($N=0,1,2,3$) was prepared as a prelude to a kinetic mechanistic study of the anation reactions of aquobromorhodate(III) complexes in aqueous acid medium (Bekker, 1968).

The first experiment was designed to examine the equilibrium hydrolysis,

$$RhBr_5(H_2O)^{2-} + Br^- \rightleftharpoons RhBr_6^{3-} + H_2O\ ,$$

as a logical complement to earlier reported studies on the chloro congeners (Robb & Harris, 1965; Robb, Steyn & Krüger, 1970). The fact that the potassium salt of the $RhBr_6^{3-}$ moiety was isolated from a liquor that yielded two other complexes of formulae $K_3Rh_2Br_9$ and $K_4Rh_2Br_{10}$ served as an indication that the kinetic picture could become rather complicated and also made it necessary that a complete characterization of the complexes be attempted.

The results of the first of these crystallographic investigations form the basis for this report. The complex of formula $K_3Rh_2Br_9$ is expected to be isomorphous with the nonachlorodirhodate(III) complex which was isolated as the quaternary ammonium salt (Work & Good, 1970). The latter complex was in turn found to be isomorphous with the chromium(III) dimeric species which was shown to exist in the solid state as two distorted octahedra coupled face to face. A more recent publication communicated the full X-ray structural analysis of the complexes $Cs_3Cr_2Br_9$, $Cs_3Mo_2Cl_9$ and $Cs_3Mo_2Br_9$ (Saillant, Jackson, Streib, Folting & Wentworth, 1971).

The complex of formula $K_4Rh_2Br_{10}$ is presently being prepared for crystallographic studies.

## Experimental section

Dark brown needles of the complex analysing according to the formula $K_8Rh_3Br_{18}.10H_2O$ were prepared from $Rh(OH)_3.3H_2O$ in the presence of HBr and KBr. The full details of other preparations of all of these aquobromorhodate(III) and bromorhodate(III) complexes, together with their ligand field spectra are to be reported elsewhere with the kinetic results.

Basing the amount of material taken (22 mg) on the formula $K_8Rh_3Br_{18}.10H_2O$, 10 ml of a 1 millimolar solution of the complex was made up in doubly distilled water and immediately subjected to a *p*H measurement at 20 °C. The *p*H was found to be 3 hence showing the presence of a single proton for each unit of above formula or, more correctly, $\frac{1}{3}$ of a proton per $RhBr_6^{3-}$ unit.

With the aid of oscillation, Weissenberg and precession photographs the crystals were determined to be orthorhombic with space group *Pbam* ($0kl$ with $k=2n$, $h0l$ with $h=2n$). Unit-cell dimensions were calculated from the accurate spot positions measured on a Hilger & Watts four circle automatic diffractometer.

Crystal data: