| | | | |
|---|---|---|---|
| Mo(1)—Mo(3) | 2.8124 (5) | 2.802 | 2.771 |
| Mo(1)—Mo(1)* | 2.6890 (7) | 2.711 | 2.737 |
| Mo(1)—Mo(2)* | 2.9108 (5) | 2.905 | 2.916 |
| Mo(1)—Mo(3)* | 3.0911 (5) | 3.072 | 3.066 |
| Mo(2)—Mo(5) | 2.7609 (5) | 2.771 | 2.800 |
| Mo(2)—Mo(4) | 2.7288 (5) | 2.741 | 2.761 |
| Mo(2)—Mo(3) | 2.8279 (5) | 2.828 | 2.837 |
| Mo(3)—Mo(4) | 2.6102 (5) | 2.642 | 2.678 |
| Mo(3)—Mo(5) | 2.6727 (5) | 2.719 | 2.726 |
| Mo(3)—Mo(5) | 2.7558 (5) | 2.760 | 2.785 |
| Mo(4)—Mo(5) | 2.7505 (5) | 2.741 | 2.768 |
| Mo(4)—Mo(5) | 2.7605 (5) | 2.776 | 2.775 |
| Mo(5)—Mo(5) | 2.8172 (7) | 2.828 | 2.825 |
| Mo(1)—O(5) | 2.043 (3) | 2.010 | 1.987 |
| Mo(1)—O(7) | 2.069 (3) | 2.099 | 2.066 |
| Mo(1)—O(4) | 2.113 (3) | 2.098 | 2.107 |
| Mo(1)—O(8) | 2.119 (3) | 2.093 | 2.084 |
| Mo(1)—O(8) | 2.122 (3) | 2.254 | 2.184 |
| Mo(2)—O(6) | 1.990 (3) | 1.881 | 1.984 |
| Mo(2)—O(1) | 2.009 (3) | 1.964 | 2.019 |
| Mo(2)—O(4) | 2.046 (3) | 2.032 | 2.022 |
| Mo(2)—O(8) | 2.110 (3) | 2.088 | 2.119 |
| Mo(2)—O(7) | 2.142 (3) | 2.135 | 2.090 |
| Mo(3)—O(3) | 2.058 (3) | 2.003 | 2.071 |
| Mo(3)—O(2) | 2.072 (3) | 1.985 | 2.096 |
| Mo(3)—O(4) | 2.067 (3) | 2.114 | 2.073 |
| Mo(3)—O(6) | 2.077 (3) | 2.109 | 2.035 |
| Mo(3)—O(8) | 2.146 (3) | 2.160 | 2.101 |
| Mo(4)—O(3) | 2.070 (3) | 2.083 | 2.053 |
| Mo(4)—O(7) | 2.066 (3) | 2.041 | 2.073 |
| Mo(4)—O(1) | 2.078 (3) | 2.071 | 2.034 |
| Mo(4)—O(5) | 2.055 (3) | 2.089 | 2.065 |
| Mo(4)—O(2) | 2.103 (3) | 2.110 | 2.107 |
| Mo(5)—O(5) | 2.055 (3) | 1.980 | 1.989 |
| Mo(5)—O(6) | 2.039 (3) | 2.022 | 2.041 |
| Mo(5)—O(2) | 2.077 (3) | 2.030 | 2.019 |
| Mo(5)—O(3) | 2.086 (3) | 2.154 | 2.127 |
| La—O(1) | 2.443 (3) | 2.459 | 2.473 |
| La—O(1) | 2.458 (3) | 2.503 | 2.506 |
| La—O(4) | 2.487 (3) | 2.497 | 2.556 |
| La—O(7) | 2.574 (3) | 2.558 | 2.601 |
| La—O(5) | 2.676 (3) | 2.775 | 2.688 |
| La—O(8) | 2.704 (3) | 2.618 | 2.709 |
| La—O(3) | 2.732 (3) | 2.781 | 2.726 |
| La—O(2) | 2.761 (3) | 2.772 | 2.807 |
| La—O(6) | 2.860 (3) | 2.957 | 2.919 |
| La—O(2) | 2.919 (3) | 3.023 | 2.873 |
| La—O(3) | 3.232 (3) | 3.163 | 3.166 |

Data were corrected for Lorentz–polarization effects and an empirical absorption correction was applied to isotropically refined data. The structure was solved with the aid of *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and subsequent difference Fourier syntheses. A refinement of the occupancy factor for the La site confirmed that it is fully occupied. All calculations were performed with the *MolEN* (Fair, 1990) programs on a Digital MicroVAX 3100.

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# A Short Dynamically Symmetrical Hydrogen Bond in the Structure of K[Mg(H0.5SO4)2(H2O)2]

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## Abstract

The Mg atoms in the title compound, magnesium potassium hydrogendisufate(3−) dihydrate, are found at the centres of symmetry at the unit cell corners and are octahedrally coordinated by two water molecules and the O atoms from four $SO_4$ tetrahedra to form infinite kröhnkite-like $Mg(H_{0.5}SO_4)_2(H_2O)_2$ chains running down the $a$ axis. The sulfate and hydrogensulfate ions are coupled to form an $(SO_4HSO_4)^{3-}$ group with $O\cdots O$ 2.478 (3) Å and with the H atom disordered around a symmetric double-minimum potential well. Crossed channels along the $a$ and $b$ axes are filled by tenfold-coordinated K atoms.

## Comment

The ternary system K$_2$SO$_4$–MgSO$_4$–H$_2$O has been studied intensively as a part of the complicated sea-water salts series (Benrath & Benrath, 1929, 1930; Benrath & Sichelschmidt, 1931). Of the few double salts formed in the system, langbeinite, K$_2$SO$_4$.2MgSO$_4$ (Zemann & Zemann, 1957), is the only 1:2 compound. In the cubic Mg$_2$(SO$_4$)$_3^{2-}$ framework structure of langbeinite the Mg atoms are coordinated by six SO$_4$ groups and every SO$_4$ tetrahedron shares its corners with four MgO$_6$ octahedra. The 1:1 salts are more numerous. The existence of anhydrous, sesqui- and dihydrate phases has been shown by the X-ray powder diffraction patterns PDF Nos 36-1499, 36-1500 and 17-484, respectively (International Centre for Diffraction Data, 1993). Leonite, K$_2$SO$_4$.MgSO$_4$.4H$_2$O (Jarosch, 1985), and picromerite, K$_2$SO$_4$.MgSO$_4$.6H$_2$O (Kannan & Viswamitra, 1965), have known structures. The four and six, respectively, water molecules entering the MgO$_6$ octahedra form an extensive network of hydrogen bonds.

In contrast, the quaternary system K$_2$SO$_4$–MgSO$_4$–H$_2$SO$_4$–H$_2$O has been investigated to a much lesser extent. The synthesis of KHSO$_4$.MgSO$_4$.2H$_2$O was first reported by Meyerhoffer & Cottrell (1901) and, to our knowledge, it is the only known double K–Mg salt reported to contain the hydrogensulfate group. The present structure investigation confirms the composition of this binary 1:1 salt and reveals that the sulfate and hydrogensulfate groups are paired, constituting a hydrogendisulfate species. The salt may be more accurately represented, therefore, by the formula K[Mg(H$_{0.5}$SO$_4$)$_2$(H$_2$O)$_2$]. Measurements of the physical properties of this interesting compound are under way.

The structure of K[Mg(H$_{0.5}$SO$_4$)$_2$(H$_2$O)$_2$], shown in Fig. 1, bears important features of two groups of sulfates. The infinite chain with the composition Mg(H$_{0.5}$SO$_4$)$_2$(H$_2$O)$_2$ has analogues in the minerals kröhnkite, Na$_2$[Cu(SO$_4$)$_2$.(H$_2$O)$_2$], talmessite, Ca$_2$[Mg(AsO$_4$)$_2$(H$_2$O)$_2$], and fairfieldite, Ca$_2$[Mn(PO$_4$)$_2$(H$_2$O)$_2$] (Hawthorne, 1985). In each of these structures the four equatorial positions in the $MO_6$ octahedra are occupied by $TO_4$ groups and the apical water molecules take part in different schemes of hydrogen bonding. A unique feature of the title double salt, however, is the stitching of the Mg(H$_{0.5}$SO$_4$)$_2$(H$_2$O)$_2$ chains into a planar sheet by the strong hydrogen bonds responsible for the formation of the hydrogendisulfate anions. These last building units are common to the ferroelectric structures of $M_3$[H(SO$_4$)$_2$] where $M$ = NH$_4$ (Suzuki & Makita, 1978), ND$_4$ (Tanaka & Shiozaki, 1981) and Na (Catti, Ferraris & Ivaldi, 1979).

The coordination polyhedron of K is a bicapped cube (King, 1970) with eight O atoms from the hydrogendisulfate groups placed at the corners of a distorted cube [K—O 2.760 (2)–3.168 (2) Å] and two *trans*-capping water O atoms at a distance of 3.218 (2) Å.
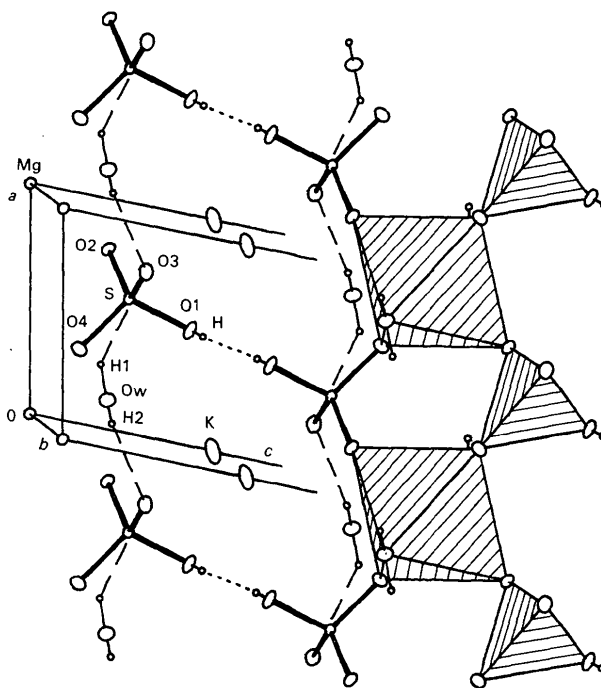


Fig. 1. Crystal structure of K[Mg(H$_{0.5}$SO$_4$)$_2$(H$_2$O)$_2$] with a segment of the kröhnkite-like chain along a. Large ellipses represent K atoms. The disordered positions of the H atoms in the hydrogendisulfate groups are connected by short dashes. Hydrogen bonds involving the water molecules at the MgO$_6$ octahedra apices are depicted by long dashes.

The K—O bond valence sum of 1.114 v.u. (Table 3), calculated according to Brown & Altermatt (1985), is in agreement with the expected univalent state of potassium. The coordination number, K—O distance range and the valence sum are consistent with the values calculated for the other mixed K–Mg sulfates: for K$_2$SO$_4$.2MgSO$_4$ (Zemann & Zemann, 1957), CN = 12/9, K—O = 2.880–3.251/2.781–3.108 Å, valence sum = 1.029/1.029 v.u.; for K$_2$SO$_4$.MgSO$_4$.4H$_2$O (Jarosch, 1985), CN = 12, K—O = 2.595–3.789 Å, valence sum = 1.052 v.u.; and for K$_2$SO$_4$.MgSO$_4$.6H$_2$O (Kannan & Viswamitra, 1965), CN = 8, K—O = 2.715–3.288 Å, valence sum = 0.927 v.u.

The Mg—O distances in the rigid octahedron cover a narrow range from 2.051 (2) to 2.069 (2) Å. The shortest distance is to O4, which is the only O atom in the structure linked to two cations (Mg and S) and which has a valence sum of 1.944 v.u. The two other chemically distinct O atoms in the coordination sphere of Mg form additional bonds with K and S (O2) and H and K (O$W$). The average bond length of 2.063 (9) Å resembles that of 2.062 (10) Å found in Mg(HSO$_4$)$_2$ (Simonov, Trojanov, Kemnitz, Hass & Kammler, 1986) and those values found in the mixed K–Mg sulfates: 2.050 (33)/2.075 (50) Å in K$_2$SO$_4$.2MgSO$_4$ (Zemann & Zemann, 1957); 2.061 (41)/2.078 (5) Å in K$_2$SO$_4$.MgSO$_4$.4H$_2$O (Jarosch, 1985); and 2.092 (29) Å

in $K_2SO_4.MgSO_4.6H_2O$ (Kannan & Viswamitra, 1965). It is noteworthy that the sum of the effective ionic radii (Shannon, 1976) of $Mg^{2+}$ (0.57 Å) and $O^{2-}$ (1.40 Å) gives an underestimate for the length of the Mg—O bonds.

The $SO_4$ tetrahedron has a trigonally distorted geometry with three distances in the range 1.459 (2)– 1.466 (2) Å and an elongated bond S—O1 of 1.509 (2) Å. This distortion is due to the formation of a short hydrogen bond S—O1···H···O1—S disposed around the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The angle S—O1···O1 of 112.46 (6)° can be compared with the values of 108.9 (2) and 114.8 (2)° in the structures of $(NH_4)_3[H(SO_4)_2]$ (Suzuki & Makita, 1978) and $Na_3[H(SO_4)_2]$ (Catti, Ferraris & Ivaldi, 1979) in which the S—O/O···O distances are 1.527 (2)/2.540 (2) and 1.518 (3)/2.434 (4) Å, respectively. An electron density map in the region of the hydrogen bond (Fig. 2) clearly shows that the H atom is disordered between two symmetry-restricted (Catti & Ferraris, 1976) positions. The uniformity of the r.m.s. amplitudes of the displacement ellipsoids of the O atoms in the $SO_4$ group suggests that the nature of the H-atom disorder is dynamical. Otherwise, an alternative static disorder of H should be reflected by increased r.m.s. amplitudes for O1 compared with the rest of the atoms in the $SO_4$ group and orientation of the displacement ellipsoid of O1 along the S—O1 bond. In the present case the longest/shortest principal axes of the displacement ellipsoid of O1 make angles of 87.0/28.2 and 88.6/39.7° with the S—O1 and O1···O1 lines, respectively. The r.m.s. amplitudes given in Table 4 are comparable with the analogous values for the structure of $KHSO_4$ (Payan & Haser, 1976).

The negatively charged sheets formed from infinite kröhnkite-like $Mg(H_{0.5}SO_4)_2(H_2O)_2$ chains lie parallel

to the diagonal (101) plane. The sheets are held together to form a three-dimensional structure by electrostatic forces between the sheets and the $K^+$ cations, and by hydrogen bonding to the water molecules.

## Experimental

*Crystal data*

| | |
|---|---|
| $KMg[H(SO_4)_2].2H_2O$ | Mo $K\alpha$ radiation |
| $M_r = 292.57$ | $\lambda = 0.71073$ Å |
| Triclinic | Cell parameters from 22 |
| $P\bar{1}$ | reflections |
| $a = 4.657$ (1) Å | $\theta = 20.19-21.89°$ |
| $b = 5.743$ (1) Å | $\mu = 1.22$ mm$^{-1}$ |
| $c = 8.214$ (1) Å | $T = 292$ K |
| $\alpha = 104.02$ (2)° | Isometric |
| $\beta = 99.94$ (2)° | $0.06 \times 0.06 \times 0.06$ mm |
| $\gamma = 95.06$ (2)° | Transparent |
| $V = 208.0$ (2) Å$^3$ | |
| $Z = 1$ | |
| $D_x = 2.335$ Mg m$^{-3}$ | |

*Data collection*

| | |
|---|---|
| Enraf–Nonius CAD-4 diffractometer | 681 observed reflections $[I > 3.0\sigma(I)]$ |
| $\omega/2\theta$ scans [width (0.80 + 0.40tan$\theta$)° in $\omega$] | $R_{int} = 0.030$ $\theta_{max} = 28.0°$ |
| Absorption correction: empirical | $h = -6 \rightarrow 6$ $k = -7 \rightarrow 7$ |
| $T_{min} = 0.914$, $T_{max} = 0.999$ | $l = -10 \rightarrow 10$ 3 standard reflections |
| 2008 measured reflections | frequency: 120 min |
| 1004 independent reflections | intensity variation: $-0.9\%$ |

*Refinement*

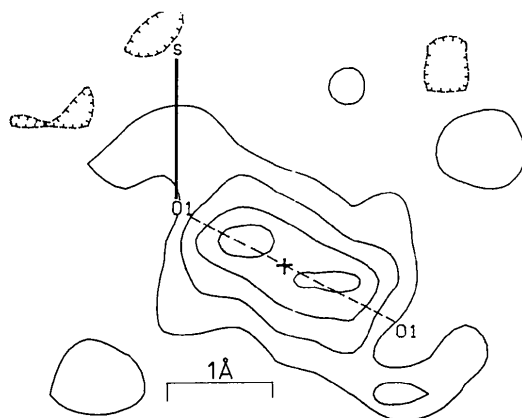| | |
|---|---|
| Refinement on $F$ | $\Delta\rho_{max} = 0.313$ e Å$^{-3}$ |
| $R = 0.026$ | $\Delta\rho_{min} = -0.380$ e Å$^{-3}$ |
| $wR = 0.029$ | Extinction correction: |
| $S = 1.020$ | $F_{c,corr} = F_c/(1 + gI_c)$ |
| 681 reflections | (Stout & Jensen, 1968) |
| 77 parameters | Extinction coefficient: |
| Only coordinates of H atoms refined | $g = 3.1434 \times 10^{-6}$ Atomic scattering factors |
| $w = 1/[\sigma^2(F) + (0.001F)^2]$ | from *SDP* (Enraf–Nonius, |
| $(\Delta/\sigma)_{max} = 0.016$ | 1985) |



Fig. 2. An electron density map showing the splitting of the electron density peak in the region of the short hydrogen bond. The structural model was refined initially with the H atom placed at the centre of symmetry. Then the H atom was omitted from the calculations of $F_c$. The plane of the difference Fourier map was defined by the atoms S and O1 and a point at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which is labelled by a cross. Contours start from 0.2 e Å$^{-3}$ with an interval of 0.2 e Å$^{-3}$.

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å$^2$)

$U_{iso}$ for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all others.

| | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| K | 0 | 0 | 1/2 | 0.0349 (3) |
| Mg | 0 | 0 | 0 | 0.0126 (3) |
| S | 0.6092 (2) | 0.3175 (1) | 0.24216 (9) | 0.0122 (1) |
| O1 | 0.5255 (5) | 0.2999 (4) | 0.4086 (2) | 0.0214 (5) |

| | | | | |
|---|---|---|---|---|
| O2 | 0.7937 (4) | 0.1259 (3) | 0.2017 (2) | 0.0190 (5) |
| O3 | 0.7619 (4) | 0.5585 (3) | 0.2657 (2) | 0.0222 (6) |
| O4 | 0.3435 (4) | 0.2732 (3) | 0.1096 (2) | 0.0194 (5) |
| OW | 0.1888 (4) | −0.2207 (3) | 0.1410 (3) | 0.0207 (5) |
| H1 | 0.335 (8) | −0.267 (7) | 0.127 (5) | 0.02533 |
| H2 | 0.086 (8) | −0.308 (7) | 0.163 (5) | 0.02533 |
| H† | 0.515 (8) | 0.385 (6) | 0.437 (5) | 0.02533 |

† 50% site occupancy.

Table 2. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| K—O1$^i$ | 3.023 (2) | K—OW$^{vii}$ | 3.218 (2) |
| K—O1 | 3.168 (2) | Mg—O2$^i$ | 2.069 (2) |
| K—O1$^{ii}$ | 3.168 (2) | Mg—O4 | 2.051 (2) |
| K—O1$^{iii}$ | 3.023 (2) | Mg—OW | 2.068 (2) |
| K—O2$^i$ | 2.760 (2) | S—O1 | 1.509 (2) |
| K—O2$^{iii}$ | 2.760 (2) | S—O2 | 1.466 (2) |
| K—O3$^{iv}$ | 2.787 (2) | S—O3 | 1.452 (2) |
| K—O3$^v$ | 2.787 (2) | S—O4 | 1.459 (2) |
| K—OW | 3.218 (2) | | |
| | | | |
| O1$^i$—K—O1 | 97.55 (6) | O2$^i$—Mg—OW | 86.76 (8) |
| O1$^i$—K—O2$^i$ | 47.95 (6) | O4—Mg—OW | 91.38 (8) |
| O1$^i$—K—O3$^{iv}$ | 99.11 (5) | O1—S—O2 | 105.1 (1) |
| O1$^i$—K—OW | 103.71 (5) | O1—S—O3 | 108.9 (1) |
| O2$^i$—K—O3$^{iv}$ | 76.10 (6) | O1—S—O4 | 109.2 (1) |
| O2$^i$—K—OW | 56.14 (6) | O2—S—O3 | 113.2 (1) |
| O3$^{iv}$—K—OW | 53.68 (6) | O2—S—O4 | 110.3 (1) |
| O2$^i$—Mg—O4 | 89.68 (8) | O3—S—O4 | 110.0 (1) |

| D | H | A | D—H | H···A | D···A | D—H···A |
|---|---|---|---|---|---|---|
| O1 | H | O1$^v$ | 0.50 (4) | 1.99 (4) | 2.478 (4) | 168 (6) |
| OW | H1 | O3$^{vi}$ | 0.77 (4) | 2.52 (4) | 3.172 (3) | 143 (4) |
| OW | H2 | O3$^{iv}$ | 0.74 (4) | 2.03 (4) | 2.738 (3) | 160 (4) |

Symmetry codes: (i) $x − 1, y, z$; (ii) $−x, −y, 1 − z$; (iii) $1 − x, −y, 1 − z$; (iv) $x − 1, y − 1, z$; (v) $1 − x, 1 − y, 1 − z$; (vi) $x, y − 1, z$.

Table 3. *Bond valences for the non-H atoms* (v.u.)

| | K | Mg | S | Sum |
|---|---|---|---|---|
| O1 | 0.090, 0.061 | | 1.365 | 1.516 |
| | 0.090, 0.061 | | | |
| O2 | 0.183 | 0.362 | 1.533 | 2.078 |
| | 0.183 | 0.362 | | |
| O3 | 0.170 | | 1.593 | 1.763 |
| | 0.170 | | | |
| O4 | | 0.380 | 1.564 | 1.944 |
| | | 0.380 | | |
| OW | 0.053 | 0.363 | | 0.416 |
| | 0.053 | 0.363 | | |
| Sum | 1.114 | 2.210 | 6.055 | |

Table 4. *Root-mean-squared atomic displacement amplitudes* (Å)

| | Minimum | Intermediate | Maximum |
|---|---|---|---|
| K | 0.134 | 0.139 | 0.256 |
| Mg | 0.098 | 0.113 | 0.117 |
| S | 0.089 | 0.110 | 0.123 |
| O1 | 0.092 | 0.126 | 0.184 |
| O2 | 0.095 | 0.138 | 0.170 |
| O3 | 0.091 | 0.145 | 0.192 |
| O4 | 0.117 | 0.120 | 0.166 |
| OW | 0.104 | 0.142 | 0.171 |

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976), *STRUPLO*84 (Fischer, 1985). Software used to prepare material for publication: *KAPPA* (Macíček, 1992, unpublished).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1069). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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