Hydrous Potassium and Ferric Iron Sulphate (Maus's Salt)*

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Abstract. Maus's salt is reported in the literature as having the chemical formula $K_5Fe_3(SO_4)_6(OH)_2 \cdot nH_2O$ where $n = 8,9$. Hexagonal, $P6_3/m$, $a = 9 \cdot 71$ (1), $c = 18 \cdot 96$ (2) Å, $Z = 2$, $D_m = 2 \cdot 412$ (Scharizer, *Z. Kristallogr.* (1923). **58**, 420–444), $D_x = 2 \cdot 437$ g cm^{-3}. The structure consists of groups $Fe_3O(H_2O)_3(SO_4)_6$, built up by three $FeO_5(H_2O)$ octahedra and six SO_4 tetrahedra. Linkages formed by one kind of K atom give a stratiform arrangement with inter-sheet connexions provided by other K atoms. There is evidence of (K, H_2O) substitution, while the presence of oxonium and hydroxyl groups is suggested by symmetry considerations.

Introduction. Short prismatic crystals of the above compound were obtained by evaporation at 70–80°C of an aqueous solution of ferric iron sulphate and potassium sulphate. Unfortunately these crystals are very unstable and quickly deteriorate if removed from the equilibrium solution. For the X-ray study a crystal ($\sim 0 \cdot 2 \times 0 \cdot 2 \times 0 \cdot 3$ mm) with its mother liquor was sealed in a Lindemann-glass capillary tube. This avoids deterioration of the crystal but has the disadvantages of X-ray absorption by the solution and the growth of secondary crystals.

Weissenberg photographs revealed the crystals to be hexagonal, belonging to the space groups $P6_3/m$ or $P6_3$, thus confirming the previous results (Beran, 1971). Unit-cell parameters were obtained from zero-level Weissenberg photographs and refined (using a least-squares method) from high-θ reflexions (Mo $K\alpha$ radiation, automatic diffractometer). Intensities were collected on a Philips PW 1100 four-circle automatic diffractometer by ω–2θ scans (scan speed $0 \cdot 04°$ s^{-1}, scan range $1 \cdot 2°$, $2° < \theta < 26°$) using Mo $K\alpha$ radiation and a graphite monochromator. A total of 1059 independent reflexions were measured. Of these, 168 weak reflexions with $(I_{top} - 2\sqrt{I_{top}}) < I_{bck}$ were omitted (I_{top} is the intensity in counts/sec measured at the maximum of the reflexion during the first scan; I_{bck}

is the mean of two 5 s preliminary background measurements). To this group of unobserved reflexions a conventional F_o value identical with the minimum measured F_o was attributed.

Intensities were corrected for Lorentz and polarization effects. The tangent formula of Karle & Karle (1966) was used to locate the heavy atoms. The structure was refined in the space group $P6_3/m$ by the full-matrix least-squares method (Busing, Martin & Levy, 1962). In the last cycles of refinement anisotropic thermal parameters were taken into account, while four reflexions (002, 0,0,10, 4,1,10, 0,0,16) were excluded because of secondary extinction effects. The final conventional R index was $0 \cdot 086$ for 887 non-zero reflexions and $0 \cdot 099$ including the unobserved reflexions. The atomic scattering factors used in this work are those given by Cromer & Waber (1965) with anomalous dispersion correction for Fe after Cromer (1965).
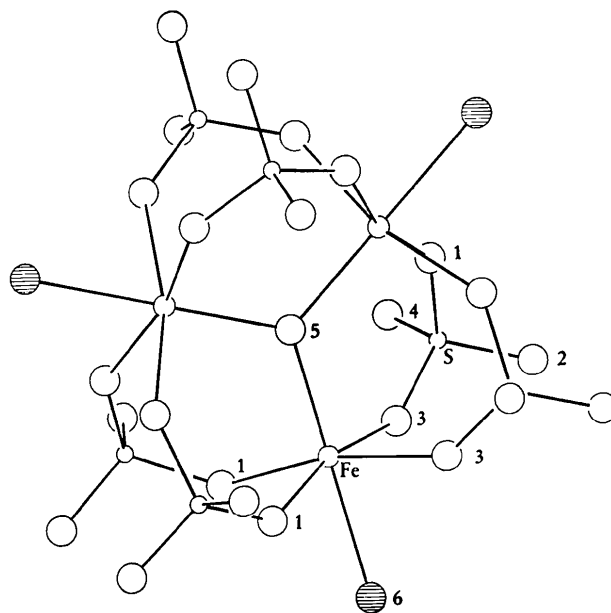

Fig. 1. A group with composition $Fe_3O(H_2O)_3(SO_4)_6$. Only oxygen atoms are numbered; hatched circles mark water oxygen atoms.

Positional and thermal parameters are listed in Table 1.*

Discussion. In the literature Maus's salt is often considered to be identical with the natural compound known as metavoltine. Recently Scordari, Vurro & Menchetti (1975), by means of X-ray and chemical investigations, showed that between the synthetic and the natural compounds there exist many similarities, but the two are not identical; the main differences are

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31006 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the space group and the presence in metavoltine of Fe''. The present paper, which describes the crystal structure of Maus's salt, is a contribution to clarify the crystal-chemical relationships between the two compounds. The crystal structure of metavoltine from Sierra Gorda, Chile, has already been determined and the related paper is now in preparation (Giacovazzo, Scordari, Todisco & Menchetti, 1975).

Selected interatomic distances and angles are given in Table 2. As shown in Fig. 1, an interesting feature is the oxygen atom O(5), lying on $\bar{6}$, which is the common vertex of three $FeO_5(H_2O)$ octahedra around the threefold axis. The configuration of O(5) is rather unusual, but has already been observed in amarantite (Süsse, 1968; Giacovazzo & Menchetti, 1969) and

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

The temperature factors refer to the expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. For atoms labelled P, Q, R see text.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	1738 (2)	2157 (2)	$\frac{1}{4}$	55 (3)	53 (3)	22 (3)	22 (2)	0	0
S	3133 (3)	609 (3)	1414 (1)	68 (3)	119 (4)	15 (3)	55 (3)	4 (1)	3 (1)
K(2)	0	0	0	128 (6)	128	36 (5)	64	0	0
K(3)	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	131 (6)	131	24 (4)	65	0	0
O(1)	884 (8)	2941 (7)	1764 (4)	139 (13)	134 (13)	59 (5)	16 (11)	−29 (6)	47 (6)
O(2)	4732 (7)	954 (9)	1465 (4)	100 (11)	309 (18)	34 (4)	116 (12)	3 (5)	−6 (6)
O(3)	2992 (9)	1848 (8)	1775 (5)	253 (18)	86 (12)	82 (6)	24 (12)	95 (7)	−15 (6)
O(4)	2687 (10)	477 (14)	699 (4)	192 (17)	825 (42)	21 (4)	270 (23)	−9 (6)	11 (9)
O(5)	0	0	$\frac{1}{4}$	48 (11)	48	10 (6)	24	0	0
$O_w(6)$	3677 (11)	4551 (9)	$\frac{1}{4}$	148 (18)	40 (13)	47 (6)	33 (12)	0	0
P	3580 (5)	4274 (5)	541 (2)	282 (10)	196 (8)	40 (4)	103 (8)	−41 (3)	−15 (3)
Q	$\frac{1}{3}$	$\frac{2}{3}$	1428 (9)	176 (19)	176	87 (10)	88	0	0
R	$\frac{1}{3}$	$\frac{2}{3}$	−180 (9)	559 (35)	559	35 (7)	279	0	0

Table 2. *Selected interatomic distances and angles with e.s.d.'s*

S–O(1^x)	1·455 (7) Å		O(1^x)–S–O(2)	111·1 (4)°
S–O(2)	1·418 (8)		O(1^x)–S–O(3)	107·0 (5)
S–O(3)	1·449 (9)		O(1^x)–S–O(4)	108·2 (5)
S–O(4)	1·409 (8)		O(2)—S–O(3)	108·5 (5)
			O(2)—S–O(4)	109·7 (5)
			O(3)—S–O(4)	112·2 (7)
Fe–O(1)	1·962 (9)	(×2)	O(1)–Fe–O(1^{xii})	90·7 (4)
Fe–O(3)	1·956 (9)	(×2)	O(1)–Fe–O(3)	88·6 (4) (×2)
Fe–O(5)	1·924 (3)		O(1)–Fe–O(3^{xii})	167·4 (2) (×2)
Fe–O$_w$(6)	2·138 (7)		O(1)–Fe–O(5)	96·4 (2) (×2)
			O(1)–Fe–O$_w$(6)	83·8 (3) (×2)
K(2)–O(4)	2·752 (10) (×6)		O(3)–Fe–O(3^{xii})	89·3 (4)
K(3)–O(2)	2·894 (7) (×6)		O(3)–Fe–O(5)	96·2 (2) (×2)
			O(3)–Fe–O$_w$(6)	83·7 (3) (×2)
O$_w$(6)–O(2^{viii})	2·953 (9) (×2)		O(5)–Fe–O$_w$(6)	179·7 (2)
P–O(2^{viii})	2·848 (7)		O(4)–K(2)–O(4^{ii})	180·0 (×3)
P–O(4^{xi})	2·760 (9)		O(4)–K(2)–O(4^v)	98·7 (4) (×6)
P–Q	2·974 (12)		O(4)–K(2)–O(4^{vii})	81·3 (4) (×6)
P–R	2·807 (9)			
Q–P	2·974 (12) (×3)		O(2)–K(3)–O(2^{iv})	79·1 (2) (×6)
Q–O$_w$(6)	3·024 (15) (×3)		O(2)–K(3)–O(2^{xii})	85·4 (2) (×3)
Q–R	3·050 (26)		O(2)–K(3)–O(2^{xiii})	136·9 (2) (×6)
R–P	2·807 (10) (×3)		O(2^{viii})–O$_w$(6)–O(2^{xv})	83·3 (3)
R–Q	3·050 (26)			

Symmetry code

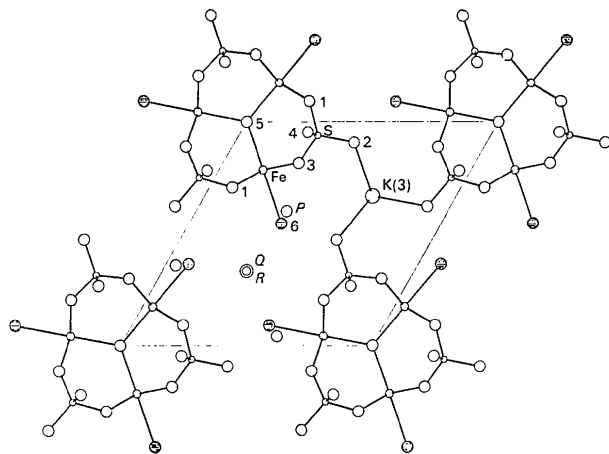|							
None	x	y	z	(viii)	$1-x+y$	$1-x$	z
(ii)	$-x$	$-y$	$-z$	(x)	$1-x+y$	$-x$	z
(iv)	$1-y$	$x-y$	z	(xi)	$x-y$	x	$-z$
(v)	$-y$	$x-y$	z	(xii)	x	y	$\frac{1}{2}-z$
(vii)	y	$-x+y$	$-z$	(xv)	$1-x+y$	$1-x$	$\frac{1}{2}-z$

Fig. 2. A sheet parallel to the xy plane at a mean $z = \frac{1}{4}$. Note that all atoms related by the mirror plane at $z = \frac{1}{4}$ are exactly overlapped (SO_4 tetrahedra, P, Q and R positions).

metavoltine from Sierra Gorda (Giacovazzo et al., 1975). Fe octahedra are connected by corner sharing to six SO_4 tetrahedra, thus forming a group of composition $Fe_3O(H_2O)_3(SO_4)_6$. These groups are at a mean z of $\frac{1}{4}$ and $\frac{3}{4}$; each group at $z = \frac{1}{4}$ is inverted with respect to the group at $z = \frac{3}{4}$. As a consequence the volumes around the two non-symmetrical positions $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ show a different density of oxygen atoms belonging to the surrounding $Fe_3O(H_2O)_3(SO_4)_6$ groups. The $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ position, corresponding to the lesser oxygen–oxygen inter-group distances, is filled by the K(3) atom which binds six O(2) symmetry-related sulphate oxygens according to a trigonal prism. The result is the formation of equidistant sheets (in the xy plane) at $z = \frac{1}{4}$ (see Fig. 2) and $z = \frac{3}{4}$. Along c the connexion of sheets into a three-dimensional framework takes place via K(2) atoms. K(2), lying on $\bar{3}$, binds six O(4) symmetry-related sulphate oxygens, belonging to two different sheets, according to a c-flattened octahedron.

The above structural description does not include the atoms labelled P, Q, R which occupy the space around $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$. It is not easy to assign definite atomic species to these labels; however, on the basis of the chemical data and of the trend of refinement, one can draw the following conclusions. According to Scharizer (1923, 1927) and Scordari et al. (1975) ten K atoms are to be expected in the unit cell; since K(2) and K(3) give a total of four atoms, six K atoms still remain to be located. Several refinement attempts, including

occupancy refinement, indicated that the position labelled P is very likely to be statistically occupied by water and potassium in a 1:1 ratio, accounting for the expected number of K atoms in the unit cell. On the basis of the chemical data and of the above definition of P, the Q and R positions should be occupied by groups (like H_2O) with zero total charge and not by K atoms. Nevertheless, because of the threefold point symmetry, these groups cannot be water molecules and it becomes necessary to admit the presence of H_3O^+ and OH^- respectively. Unfortunately the quality of the experimental data did not permit a direct determination of the H atom positions. Some difficulties arise in analysing the interatomic distances and coordination involving P, Q, R (see Table 2); nevertheless the previous solution seems to be the only one which is consistent with the requirements of both the chemical formula and the electrostatic valence neutrality. It is very likely that from these weak points a breakdown of the structural arrangement takes place, thus accounting for the well known instability of Maus's salt. The structure explains the perfect $\{0001\}$ cleavage.

According to the present results the crystal chemical formula of Maus's salt should be written:
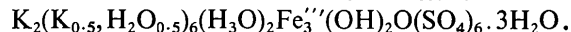
$$K_2(K_{0.5}, H_2O_{0.5})_6(H_3O)_2Fe_3'''(OH)_2O(SO_4)_6 . 3H_2O .$$

References

BERAN, A. (1971). Neues Jb. Miner. Mh. pp. 89–90.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS. Oak Ridge National Laboratory Report ORNL-TM-305.
CROMER, D. T. (1965). Acta Cryst. 18, 17–23.
CROMER, D. T. & WABER, J. T. (1965). Acta Cryst. 18, 104–109.
GIACOVAZZO, C. & MENCHETTI, S. (1969). Rend. Soc. Ital. Miner. Petr. 26, 399–406.
GIACOVAZZO, C., SCORDARI, F., TODISCO, A. & MENCHETTI, S. (1975). In preparation.
KARLE, J. &. KARLE, I. L. (1966). Acta Cryst. 21, 849–859.
SCHARIZER, R. (1923). Z. Kristallogr. 58, 420–444.
SCHARIZER, R. (1927). Z. Kristallogr. 65, 1–22.
SCORDARI, F., VURRO, F. & MENCHETTI, S. (1975). Tschermaks Miner. Petrogr. Mitt. 22, 88–97.
SÜSSE, P. (1968). Z. Kristallogr. 127, 261–275.