The Structure of
$K_2(K_{0.41},H_2O_{0.59})_6Na_{3.98}H_3O^+_{0.78}X^+_{0.68}(Fe^{2+}_{0.05},\square_{0.95})Fe^{3+}_6O_2(SO_4)_{12} \cdot 11 \cdot 91H_2O$: a Compound Related to Metavoltine and α-Maus's Salt

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Abstract

A synthetic phase, obtained by complete evaporation at about 353 K of an aqueous solution containing iron(III), hydrated sodium sulfates and potassium sulfate, has been found to be an interesting compound related to metavoltine, $K_2Na_6(Fe^{2+},Cu,Zn)Fe^{3+}_6O_2(SO_4)_{12} \cdot 18H_2O$, and to α-Maus's salt, $K_5Fe^{3+}_3O(SO_4)_6 \cdot 10H_2O$. The occupancy coefficients lead to structure models in agreement with space group $P1$, although the structure of this compound has been solved in $P3$. Lattice parameters are $a = b = 9 \cdot 643$, $c = 18 \cdot 018$ Å, and $Z = 1$. The crystal structure has been determined from X-ray data collected on an automated diffractometer by means of Patterson and Fourier syntheses. The least-squares refinement using 2542 observed reflections led to a conventional R value of $0 \cdot 086$ with isotropic temperature factors. Like metavoltine and α-Maus's salt, the present structure is based on $[Fe^{3+}_3(H_2O)_3O(SO_4)_6]^{5-}$ clusters which are essentially linked to each other by alkaline ions and hydrogen bonds. As in α-Maus's salt, some sites are statistically occupied by K atoms and water molecules forming rings around the trigonal axis, while as in metavoltine, one site is occupied by an Fe^{2+} cation; this site appears to be much less occupied in the present salt.

Introduction

This study was undertaken to obtain a more complete crystal-chemical knowledge of a group of natural and synthetic compounds whose structures are based on $[Fe^{3+}_3(H_2O)_3O(SO_4)_6]^{5-}$ units, as in metavoltine (Scordari, Vurro & Menchetti, 1975; Giacovazzo, Scordari, Todisco & Menchetti, 1976) and α-Maus's salt (Giacovazzo, Scordari & Menchetti, 1975).

Blaas (1883) claimed that metavoltine from Madeni Zakh, Iran, and α-Maus's salt were very similar. Consequently, he assigned them the general formula $5RO.3Fe_2O_3.12SO_3.18H_2O$ where RO is (K_2O,Na_2O,FeO) in metavoltine and K_2O in α-Maus's salt.

According to these results, Palache, Berman & Frondel (1951) proposed the following chemical formula for metavoltine: $(K,Na,Fe^{2+})_5Fe^{3+}_3(SO_4)_6.9H_2O$ (?), specifying that 'Na and apparently also Fe^{2+} substitute for K, with Na > K in some material'.

These conclusions were confuted by Giacovazzo *et al.* (1976). They stated that metavoltine and α-Maus's salt could be considered two different compounds either because of their topology or because of the presence of Fe^{2+} in metavoltine.

The compound examined here, hereafter referred to as 'salt X', is related to metavoltine in its topology and to α-Maus's salt in its chemistry. This study allows us to interpret, from a general crystallographic point of view, the apparent Na, Fe^{2+} and K 'diadochy' mentioned by Palache *et al.* (1951) and to understand how these replacements influence the cluster orientation.

Experimental

According to Van Tassel's (1961) recipe, the crystals used for this study were obtained by evaporation (at about 353 K) from a solution containing $K_2SO_4(0 \cdot 6$ g), $Na_2SO_4.10H_2O$ (3·4 g) and $Fe_2(SO_4)_3.nH_2O$ (4·3 g) (for details see Scordari, 1977). These crystals are very similar to those of metavoltine in colour, cleavage and optical properties as well as in unit-cell dimensions and space groups. This suggests that the two compounds have similar chemical formulae. No usual chemical analysis was performed before starting the structural study. In fact, owing to the large replacement showed by similar compounds as regards the alkaline and hydronium ions (Scordari *et al.*, 1975; Scordari, 1977), we were discouraged from establishing the exact Na, K and H_3O^+ content. Of course, the replacement affects the unit-cell parameters; for instance, two crystals from the same batch show the following lattice constants: $a = b = 9 \cdot 64$, $c = 18 \cdot 02$ Å, and $a = b = 9 \cdot 60$, $c = 18 \cdot 81$ Å.

The crystal studied here had previously been lacquered and investigated by Weissenberg photographs (exposed for ~30h), to verify the symmetry and its suitability for the structural study.

Intensity data were collected from a small, short, prismatic hexagonal crystal ($0\cdot10 \times 0\cdot10 \times 0\cdot15$ mm) using a Philips PW 1100 single-crystal automated diffractometer (at the Istituto di Mineralogia dell'Università di Perugia, Italy) with graphite-monochromatized Mo $K\alpha$ radiation. A total of 3251 independent reflections were measured up to $\theta = 30°$. Of these, 709 with $(I - 2\sqrt{I}) < B$ were considered unobserved (I is the intensity in counts s^{-1} measured at the peak position of the reflection during the first scan; B is the mean of two background measurements of 10 s each). Three standard reflections were measured at 3 h intervals and showed no appreciable variations in intensity. The intensities were corrected for Lorentz–polarization effects, but not for absorption ($\mu = 2\cdot43$ mm^{-1}).

Structure determination and refinement

A Patterson synthesis confirmed the reasonable assumption that the structure was based on

Table 1. *Fractional atomic coordinates and isotropic thermal parameters with their standard deviations*

Site	Occupancy	x	y	z	B (Å²)
Refined positional and thermal parameters					
Fe(1)	1·0	0·4464 (2)	0·1657 (2)	0·7313 (1)	0·87 (2)
S(1)	1·0	0·4120 (3)	0·4050 (3)	0·8422 (1)	1·69 (4)
S(2)	1·0	0·4324 (3)	0·4040 (3)	0·6121 (1)	1·37 (4)
K	1·0	$\frac{1}{3}$	$\frac{2}{3}$	0·7251 (3)	2·79 (8)
Na(1)	1·0	$\frac{1}{3}$	$\frac{2}{3}$	0·5167 (4)	2·00 (12)
O(1)	1·0	$\frac{2}{3}$	$\frac{1}{3}$	0·7310 (6)	1·37 (19)
O(2)	1·0	0·3953 (10)	0·2459 (10)	0·8247 (4)	2·11 (13)
O(3)	1·0	0·3615 (9)	0·2793 (9)	0·6725 (4)	1·67 (11)
O(4)	1·0	0·5937 (10)	0·5300 (10)	0·6388 (4)	2·36 (14)
O(5)	1·0	0·5377 (10)	0·5275 (10)	0·7922 (4)	2·37 (14)
Ow(6)	1·0	0·7809 (11)	0·7993 (11)	0·7308 (5)	2·61 (15)
O(7)	1·0	0·3292 (10)	0·4729 (10)	0·6038 (4)	1·99 (13)
O(8)	1·0	0·5524 (11)	0·6676 (11)	0·4554 (4)	2·50 (15)
O(9)	1·0	0·2635 (12)	0·4035 (12)	0·8252 (5)	3·06 (17)
O(10)	1·0	0·5433 (13)	0·5559 (13)	0·0799 (5)	3·79 (20)
P(11)*	1·0	0·1854 (8)	0·1682 (8)	0·4320 (3)	2·68 (15)
Unrefined positional and thermal parameters					
Fe(2)	0·05 (0)	0·0	0·0	0·5	1·0
Na(2)	0·06 (2)	0·161	0·426	0·951	2·0
Na(3)	0·16 (2)	0·415	0·265	0·034	2·0
Na(4)	0·15 (2)	0·256	0·429	0·047	2·0
Na(5)	0·29 (2)	0·431	0·148	0·972	2·0
H₃O(1)	0·66 (3)	0·0	0·0	0·148	2·4
H₃O(2)	0·12 (3)	0·0	0·0	0·850	2·4
Ow(12)	0·45 (2)	$\frac{1}{3}$	$\frac{2}{3}$	0·996	2·0
Ow(13)	0·69 (2)	$\frac{2}{3}$	$\frac{1}{3}$	0·014	2·0
Ow(14)	0·16 (3)	0·215	0·045	0·942	2·4
Ow(15)	0·22 (4)	0·070	0·250	0·937	2·4
Ow(16)	0·30 (4)	0·256	0·182	0·053	2·4
Ow(17)	0·60 (3)	0·281	0·279	0·059	2·4
Ow(18)	0·29 (3)	0·275	0·050	0·950	2·4

* Site P(11) is water and K statistically distributed.

Table 2. *Interatomic distances* (Å) *and their standard deviations in parentheses*

Fe(1)—O(1)	1·921 (2)		Na(4)—O(2,5)	2·49*	
—O(2)	2·014 (8)		—O(10)	2·48*	
—O(3)	1·972 (8)		—O₁(10,2)‡	2·56*	
—O(4,1)†	2·005 (9)		—O(10,3)	2·95*	
—Ow$_{II}$(6,1)‡	2·135 (11)		—Ow(12)	2·22*	
			—Ow(15)	2·65*	
S(1)—O(2)	1·495 (10)		—Ow(16)	2·38*	
—O(5)	1·498 (10)				
—O(9)	1·457 (12)		Na(5)—O(2)	2·89*	
—O(10,3)	1·460 (10)		—O$_{II}$(10,1)‡	2·53*	
			—O(10,3)	2·89*	
S(2)—O(3)	1·509 (8)		—O(10,4)	2·37*	
—O(4)	1·496 (10)		—Ow(13)	2·21*	
—O(7)	1·455 (10)		—Ow$_{II}$(15,2)‡	2·36*	
—O(8,3)	1·441 (9)		—Ow(16)	2·37*	
K—O(7) ×3	2·863 (9)		H₃O(1)—Ow(6,3) ×3	2·98*	
—O(9) ×3	2·905 (11)		—Ow(16) ×3	2·79*	
Na(1)—O(7) ×3	2·425 (10)		—Ow(17) ×3	3·13*§	
—O(8) ×3	2·380 (10)		H₃O(2)—Ow(6,2) ×3	2·95*	
			—Ow(14) ×3	2·52*	
Fe(2)—P(11) ×6	2·11*				
			P(11)—O(3,5)	3·14*	
Na(2)—O(9)	2·53*		—O(4,3)	2·88*	
—O(10,2)	2·82*		—Ow(6,3)	2·95*	
—O(10,3)	2·51*		—O(7,4)	2·97*	
—O₁(10,5)‡	2·82*		—O(8,2)	3·12*	
—Ow(12)	2·22*		—O(8,3)	3·00*	
—Ow₁(14,1)‡	2·49*		—P(11,4) ×2	2·99*	
—Ow(17)	2·96*				
Na(3)—O(9,4)	2·79*				
—O(10)	2·57*				
—O$_{II}$(10,1)‡	2·95*				
—O(10,3)	2·58*				
—Ow(13)	2·20*				
—Ow(14)	2·62*				
—Ow(18)	2·36*§				

* Distances involving atoms with unrefined positional parameters.

† The second number in parentheses is the symmetry code according to the scheme:

none	$x,$	$y,$	z	(3)	$\bar{x},$	$\bar{y},$	$\bar{z}$
(1)	$\bar{y},$	$x - y,$	z	(4)	$y,$	$y - x,$	z
(2)	$y - x,$	$\bar{x},$	z	(5)	$x - y,$	$x,$	$\bar{z}.$

‡ Indicates atoms of adjacent cells: the translation operation is $-\mathbf{a}$(I) or $-\mathbf{b}$(II).

§ In agreement with the occupancy coefficient, the coordination number according to Na(3) and H₃O(1) is six. So to the Na(3) polyhedron may be contributed either Ow(14) or Ow(13), while to H₃O(1) either Ow(16) or Ow(17).

$[Fe_3^{3+}(H_2O)_3O(SO_4)_6]^{5-}$ clusters. Positional parameters of the atoms belonging to these clusters provided the starting input for the first structure factor and successive Fourier syntheses computations, $P\bar{3}$ being assumed. This led to an R value of $0\cdot11$ and successive attempts to locate the remaining atoms by Fourier difference maps failed to reveal significant residuals. When $P3$ was employed, additional structurally meaningful peaks were observed in the difference

Table 3. *Bond angles* (°) *and their standard deviations in parentheses*

O(1)–Fe(1)–O(2)	93·4 (4)	O(2)–S(1)–O(5)	108·2 (5)
O(1)–Fe(1)–O(3)	97·0 (3)	O(2)–S(1)–O(9)	110·2 (6)
O(1)–Fe(1)–O(4,1)*	93·5 (4)	O(2)–S(1)–O(10,3)	109·5 (6)
O(1)–Fe(1)–O(5,1)	97·7 (3)	O(5)–S(1)–O(9)	106·5 (6)
O(1)–Fe(1)–Ow(6,1)†	179·2 (3)	O(5)–S(1)–O(10,3)	110·9 (6)
		O(9)–S(1)–O(10,3)	111·5 (6)
O(2)–Fe(1)–O(3)	89·2 (3)		
O(2)–Fe(1)–O(4,1)	173·1 (5)	O(3)–S(2)–O(4)	106,7 (5)
O(2)–Fe(1)–O(5,1)	88·6 (3)	O(3)–S(2)–O(7)	107,3 (5)
O(2)–Fe(1)–Ow(6,1)†	86·6 (4)	O(3)–S(2)–O(8,3)	109·9 (5)
O(3)–Fe(1)–O(4,1)	90·4 (3)	O(4)–S(2)–O(7)	109·4 (5)
		O(4)–S(2)–O(8,3)	110·4 (6)
O(3)–Fe(1)–O(5,1)	165·2 (4)	O(7)–S(2)–O(8,3)	112·8 (5)
O(3)–Fe(1)–Ow(6,1)†	82·1 (4)		
O(4,1)–Fe(1)–O(5,1)	90·0 (4)	O(7)–Na(1)–O(7,1)	82·6 (3)
O(4,1)–Fe(1)–Ow(6,1)†	86·5 (4)	O(7)–Na(1)–O(8)	87·1 (3)
O(5,1)–Fe(1)–Ow(6,1)†	83·1 (4)	O(7)–Na(1)–O(8,2)	88·6 (3)
		O(7)–Na(1)–O(8,1)	167·3 (4)
		O(8)–Na(1)–O(8,2)	100·2 (4)

* The second number in parentheses refers to the symmetry code of Table 2.

† Indicates atoms of adjacent cells.

Fourier maps. In this Fourier synthesis, unobserved reflections were introduced but only reflections with $|F_o| < 2|F_c|$ were retained. The new peaks were in agreement with the structure's steric and electrostatic requirements and provided the final atomic coordinates for H_3O^+, Fe^{2+} and Na, as well as some other water molecules. Finally, as in α-Maus's salt, a site labelled P in Table 1 and Fig. 2 has been found to be filled statistically by K and water molecules. At this stage another least-squares cycle with isotropic thermal parameters reduced the R value to 0·069. However, some difficulties arose and cast some doubts on these encouraging results. These difficulties were: (a) some short S–O distances, such as S(1)–O(9) = 1·39 and S(2)–O(8) = 1·41 Å; (b) a bad, disordered model (built from H_3O^+, Fe^{2+} and partly from K, Na and H_2O) owing either to the high thermal parameters or to the excessive displacement of some positional parameters. After several attempts we preferred to fix the coordinates of the atoms refined in $P3$ and then to proceed to refine in $P\bar{3}$ the occupancy coefficients of all the other atoms deduced from the Fourier map and steric considerations. This improved the R index to 0·086 and gave the occupancies of statistical atoms for the drawings shown in Fig. 2. According to these sketches, $P\bar{1}$ seems the more probable space group and, consequently, the triad axis a statistical axis. In reality we tried to build models in agreement with $P3$ and the refined occupancy coefficients, but every attempt failed.

Thus, the positional parameters in Table 1 refer to: (1) a centrosymmetrical ordered unit for which the standard deviations are given and (2) a noncentrosymmetric statistical distribution of atoms with their

occupancies. Interatomic distances and angles are shown in Tables 2 and 3.*

Discussion

In agreement with the final structural results, as well as for the sake of a clearer description, we prefer to split the cell contents into two parts: the centrosymmetrical and ordered part which we call an 'ordered structure', and the noncentrosymmetrical and disordered part which we describe as a 'defect structure'.

Fig. 1 illustrates the ordered structure with chemical composition $[Na_2K_2Fe_6O_2(H_2O)_6(SO_4)_{12}]^{6-}$. It is built from two Fe–O–S complexes, two Na and two K centrosymmetrically related atoms. On the whole, this unit is similar to that found in metavoltine. However, in salt X the cluster is orientated differently; this difference involves an angle of about 25°. In this structure, O(1), shared by three Fe^{3+} cations, lies on the threefold axis. The ternary symmetry found here is also present in α-Maus's salt and metavoltine. In contrast, this symmetry is lost in β-K_5Fe_3-$O(SO_4)_6 \cdot 10H_2O$, (Mereiter & Völlenkle, 1978) in which the cluster has a pseudobinary symmetry. In our compound, O(1) and three symmetrically related Fe(1) atoms are on the same plane with an Fe(1)–O(1) distance of 1·92 Å. This distance has been found in α-Maus's salt and analogous distance are met in some carboxyl basic iron(III) complexes (Holt, Holt, Tucker, Asplund & Watson, 1972) and in β-Maus's salt

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35110 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
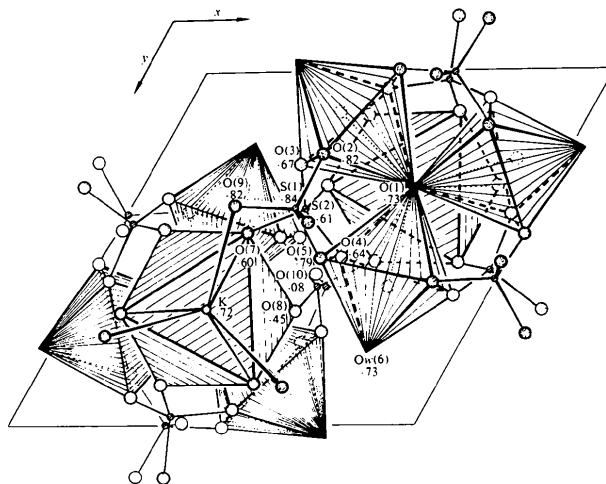

Fig. 1. The centrosymmetrical part of the structure which serves as the 'ordered structure'. This is composed of two clusters of $[Fe_3^{3+}(H_2O)_3O(SO_4)_6]^{5-}$ and two Na and two K polyhedra.

(Mereiter & Völlenkle, 1978). If we consider the mid-point between O(1) and Ow(6), Fe^{3+} is displaced in α-Maus's salt by about 0·11 Å towards O(1) and in β-Maus's salt by about 0·08 Å.

Two independent SO_4 tetrahedra furnish the rest of the O atoms to complete the Fe octahedron. In our structure there are two longer and two shorter S–O distances with mean values of 1·50 and 1·45 Å. As in some other structures the longer distances refer to those O atoms shared by S and Fe^{3+} atoms.

Two centrosymmetrical $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ complexes are connected to each other by two centrosymmetrical Na and K polyhedra lying on a threefold axis. Na atoms are octahedrally surrounded by six O atoms belonging to SO_4 groups and share a face with K polyhedra which exhibit a slightly distorted trigonal-prismatic coordination. The unit represented in Fig. 1 fills almost all the cell with the lower point at $z = 0·08$ represented by O(10) and the upper point at $z = 0·92$ represented by the centrosymmetrically related atom.
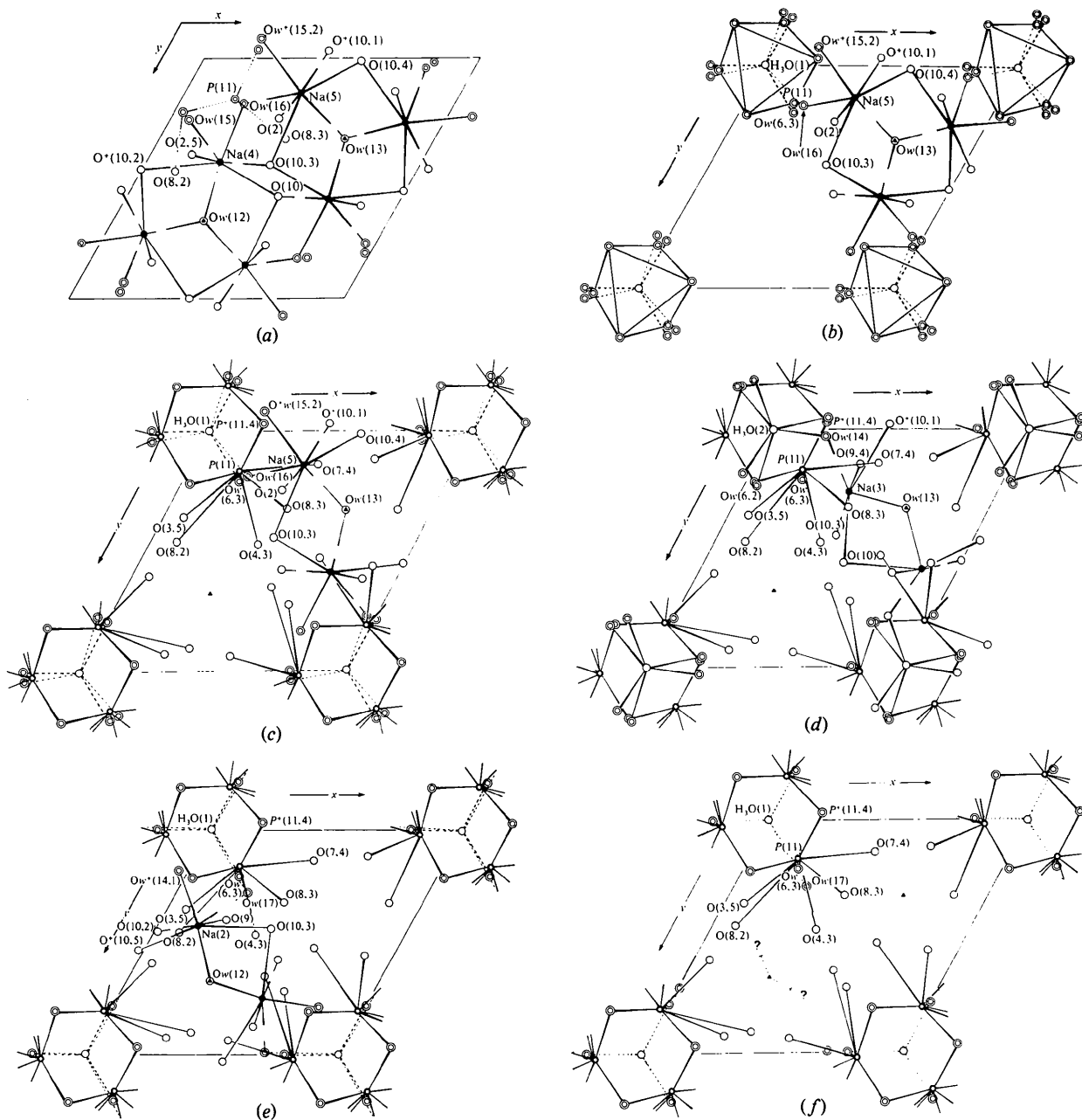

Fig. 2. The noncentrosymmetrical part which completes the structure, behaving as a 'defect structure'. This is composed of Na (filled circles), H_3O and K. According to the occupancies quoted in Table 1 the percentages proposed for (a), (b), (c), (d), (e) and (f) are: 15, 5, 13, 24, 9 and 34% respectively.

The space around the threefold axis at $(0.0,0.0,z)$, and that not filled by the unit just described, is reserved for atoms belonging to the defect structure. The latter presents fully occupied sites and others occupied only in part. The sites shared by K and water molecules (at $0.18,0.17,0.43$) are fully occupied and, according to the occupancy coefficient, the ratio is 0.7. This peculiarity is also present in α-Maus's salt for which a ratio of $1:1$ was attributed in agreement with its centrosymmetric structure. The partially filled sites concern H_3O^+, Fe^{2+} and some Na and H_2O atoms. Na and Fe^{2+} atoms were easily recognized by interatomic distances and geometrical considerations. H_3O^+, however, was identified differently: the bond distances indicated H_3O^+ or K^+ as possible cations but an attempt to refine the occupancy coefficient using K^+ instead of H_3O^+ ions was unsatisfactory. In fact, the results of the occupancy refinement were in conflict with indications from the difference synthesis. The occupancy refinement negated the existence of the K atom at $(0.0,0.0,0.85)$, contrary to the information given by the synthesis. This led us to place the H_3O^+ ion at this site and also to assume another identical ion at the site 'centrosymmetrically' related to the first. The refinement process for detecting the disordered atoms converges to 5.32 positive charges against the six expected. So the electrostatic-balance calculation showed an electrical-charge difference of $+0.68$ between the expected and found cations. These cations not directly found in the structure have been indicated by X^+ in the chemical formula. If the occupancy coefficients reported in Table 1 are taken into account, several models may be proposed. These are sketched in Fig. 2 with the following calculated percentages: 15, 5, 13, 24, 9 and 34%. The question marks in Fig. 2(f) indicate the disordered atoms (X^+) not located in the refinement step.

Finally, if we consider as waters those O atoms not belonging to the SO_4 tetrahedra, then there are 15.45 water molecules in the structure.

Comparison with α-Maus's salt and metavoltine

Our crystal-structure analysis reveals analogies and differences with respect to metavoltine from Sierra Gorda and α-Maus's salt. The main atomic frame is similar: all three structures consist of $[Fe_3^{3+}(H_2O)_3\text{-}O(SO_4)_6]^{5-}$ complexes connected by K atoms to form sheets in the xy plane. There are two such sheets per unit cell (at $z \simeq 0.25$ and $z \simeq 0.75$) which are differently related and dissimilarly interconnected in each structure. In metavoltine and in salt X there is one sheet shifted by $\frac{2}{3}a$, $\frac{1}{3}b$ with respect to the other and coupled with a mutual rotation of $60°$. However, these couplings of sheets present in both salts are oriented differently: the difference involves an angle of about

$25°$ in the xy plane. In α-Maus's salt, two clusters of the two adjacent sheets are opposed to each other with a mutual rotation of $60°$. The connection between these sheets differs in all three structures. The first sheet $(z \simeq 0.25)$ is directly linked to the second $(z \simeq 0.75)$ by two centrosymmetrical Na distorted octahedra sharing a face with K polyhedra in salt X and in metavoltine (as shown in Fig. 1). The sites reserved for Na in these salts are probably filled by H_2O in α-Maus's salt. Other K atoms, partly replaced by waters, indirectly contribute to reinforce the cohesion between these sheets in α-Maus's salt and in salt X, while Fe^{2+} atoms carry out the same function in metavoltine. Finally the connection between the second $(x \simeq 0.75)$ and the first sheet $(z \simeq 0.25)$ is the same as that just described in α-Maus's salt, owing to the centre of symmetry. In metavoltine it takes place via Na atoms, and in salt X via Na and H_3O^+.

This general comparison, although useful in identifying important differences and analogies among these structures, does not allow us to go into some particular details, which are the key to understanding some specific and close relationships between metavoltine and salt X. If we refer to six positive charges (constituted by the following atomic species: K, Na, H_3O^+, Fe^{2+}) which are the variables of the two structures, we observe that these are distributed differently in both frameworks. There is a sort of 'pouring out' of charges from the threefold axis of metavoltine at $(0.0,0.0,z)$ in the frame of the synthetic compound. In fact, in metavoltine, there are two sites at $(0.0,0.0,0.04)$ and $(0.0,0.0,0.50)$ which are fully filled by Na and Fe^{2+}. In salt X there are three sites at $(0.0,0.0,0.15)$, $(0.0,0.0,0.85)$ and $(0.0,0.0,0.50)$ partially filled by H_3O^+, H_3O^+ and Fe^{2+}, respectively, with a total charge of $+0.88$ (see Fig. 3). The remaining charges up to six are distributed among the sheets.

In the light of our structural results, the crystal-chemical formula quoted in *Dana's System of Mineralogy* (Palache, Berman & Frondel, 1951), as
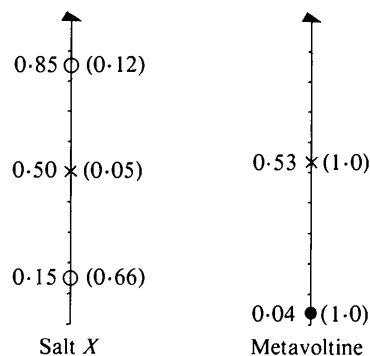
0.85 ⊕ (0.12)

0.50 ✕ (0.05)   0.53 ✕ (1.0)

0.15 ⊕ (0.66)

0.04 ● (1.0)

Salt X Metavoltine

Fig. 3. Percentage occupancies (in parentheses) and related z coordinates concerning the 'threefold' axes at $(0.0,0.0,z)$ for salt X and metavoltine. The open circles represent H_3O^+, the cross Fe^{2+} and the filled circle Na.

regards the replacements among K, Na and Fe^{2+} in the structure of metavoltine, takes on a precise significance. That is, the replacements are not the usual isomorphism among K, Na and Fe^{2+}, but a more complicated substitution among K, Na, H_3O^+ and Fe^{2+}. This distinction is similar to the problem which arose from two crystal-structure determinations of two copiapites: a magnesian copiapite (Süsse, 1972) and a ferrian copiapite (Fanfani, Nunzi, Zanazzi & Zanzari, 1973). The two structures showed deviations in the reciprocal orientations of octahedra and tetrahedra. It may be that the X site at (0·0,0·0,0·0) which is filled by divalent or trivalent cations plays an important role in affecting the system of hydrogen bonding which is quite different in the two structures. In our case we have a different distribution of positive charges in the structure compared with that of metavoltine. In fact, the iron(II) present in metavoltine is replaced by monovalent cations according to $Fe^{2+}\rightarrow2M^+$ (M is H_3O^+ or Na). This crystal-chemical difference seems to produce an important consequence on the rotation of the clusters of about 25° compared with those of metavoltine. According to Fanfani et al. (1973), the magnesian and the ferrian copiapite may be typical structures connected with the atomic species present in the mineral or two polymorphic forms. Since this problem has not yet been solved, we are still working with similar compounds in order to clarify this question. Furthermore, as happens for copiapite, it is possible that in nature there exist more than one 'metavoltine' with different chemical formulae and different structures.

Crystal chemistry and conclusions

As previously stated, the synthetic compound was crystallized from an aqueous solution containing Na^+, K^+ and Fe^{3+} sulphates. The structural result leads to a chemical formula which also contains the Fe^{2+} cation. Owing to the very low amount of this cation it seems reasonable to suspect that it comes from the impurities present in the original substance [about 0·015% of Fe^{2+} salt in $Fe_2(SO_4)_3.nH_2O$]. The stoichiometric formula deduced from the structural analysis is:
$K_{4.46}Na_{3.98}H_3O^+_{0.78}X^+_{0.68}Fe^{2+}_{0.05}Fe^{3+}_6O_2(SO_4)_{12}\cdot 15\cdot45\,H_2O$.

Taking into account the sites filled by cations and comparing this formula with those of metavoltine and α-Maus's salt, we may rearrange it in another way,

stressing some useful crystal-chemical features: $K_2(K_{0.41},H_2O_{0.59})_6Na_{3.98}H_3O^+_{0.78}X^+_{0.68}(Fe^{2+}_{0.05},\square_{0.95})Fe^{3+}_6O_2(SO_4)_{12}\cdot11\cdot91H_2O$. Now, if we compare this formula with those of metavoltine and α-Maus' salt:

α-Maus's salt:*
$$K_4(K_{0.5},H_2O_{0.5})_{12}Fe^{3+}_6O_2(SO_4)_{12}\cdot14H_2O,$$
metavoltine:
$$K_2Na_6(Fe^{2+},Cu,Zn)Fe^{3+}_6O_2(SO_4)_{12}\cdot18H_2O,$$

we may draw some interesting conclusions. Except for the small amount of Fe^{2+}, the salt X has the same chemical composition as α-Maus's salt in which part of the K^+ is replaced by H_3O^+ and Na^+. Similar chemistry may also be observed between metavoltine and salt X: some Na^+ and Fe^{2+} are replaced by H_3O^+ and Na^+ ions. Moreover, the topology of our crystal is about the same as that of metavoltine. Both the compound studied here and (K,Na) α-Maus's salt have been grown in approximately the same P/T conditions. In the attempt to find the physicochemical parameters for metavoltine also, we are continuing our effort to obtain this mineral artificially.

References

BLAAS, J. (1883). Akad. Wiss. Wien, 87, 141–163.

FANFANI, L., NUNZI, A., ZANAZZI, P. F. & ZANZARI, A. R. (1973). Am. Mineral. 58, 314–322.

GIACOVAZZO, C., SCORDARI, F. & MENCHETTI, S. (1975). Acta Cryst. B31, 2171–2173.

GIACOVAZZO, C., SCORDARI, F., TODISCO, A. & MENCHETTI, S. (1976). Tschermaks Mineral. Petrogr. Mitt. 23, 155–166.

HOLT, E. M., HOLT, S. L., TUCKER, W. F., ASPLUND, R. O. & WATSON, K. J. (1972). J. Am. Chem. Soc. 96, 2621–2623.

MEREITER, K. & VÖLLENKLE, H. (1978). Acta Cryst. B34, 378–384.

PALACHE, C., BERMAN, H. & FRONDEL, C. (1951). Dana's System of Mineralogy. New York: John Wiley.

SCORDARI, F. (1977). Mineral. Mag. 41, 371–374.

SCORDARI, F. (1980). Tschermaks Mineral. Petrogr. Mitt. In the press.

SCORDARI, F., VURRO, F. & MENCHETTI, S. (1975). Tschermaks Mineral. Petrogr. Mitt. 22, 88–97.

SÜSSE, P. (1972). Z. Kristallogr. 135, 34–55.

VAN TASSEL, R. (1961). Bull. Inst. R. Sci. Nat. Belg. Sci. Terre, 37, 1–11.