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The Structure of $K_3(K_{0.333},H_2O_{0.667})_6Na_2(Na_{0.38},H_3O^+_{0.12},H_2O_{0.50})_6Fe^{3+}_6O_2(SO_4)_{12}\cdot6H_2O$ and Its Relationship with the Parent Compound*

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Abstract

The spontaneous solid-state transformation of a hydrated iron sulphate related to metavoltine and α-Maus's salt is studied here ($R\bar{3}$, $a = 18.225$ Å, $\alpha = 30.515°$, $Z = 1$; $R = 0.079$ for 1607 reflexions). This transformation is a topotactic reaction in which the solid product is formed by a translation of adjacent sandwich sheets, $[Na_2K_2Fe^{3+}_6O_2(SO_4)_{12}(H_2O)_6]^{6-}$, by $\frac{1}{3}$ in the $\mathbf{a} + \mathbf{b}$ crystallographically equivalent orientation relative to the parent crystal. Thus, the reaction product has similar a and b parameters and c is three times that of the reactant lattice. The mechanism mainly involves a resettlement of Na atoms, reducing their coordination number, and the partial removal of water molecules.

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Introduction

Recently the crystal structure of a synthetic compound with chemical formula $K_2(K_{0.41},H_2O_{0.59})_6Na_{3.98}$-$H_3O^+_{0.78}X^+_{0.68}(Fe^{2+}_{0.05},\square_{0.95})Fe^{3+}_6O_2(SO_4)_{12}\cdot11.91H_2O$ has been solved (Scordari, 1980a). This compound, 'salt X', has been obtained from a solution containing K_2SO_4 (0.6g), $Na_2SO_4\cdot10H_2O$ (3.4g) and $Fe_2(SO_4)_3\cdot nH_2O$ (4.3g), at about 353 K. These crystals are not stable under standard conditions and gradually change into other crystals, which are related to the parent crystals in symmetry and lattice parameters. The solid-state reaction has been revealed accidentally by two successive X-ray powder patterns, which were carried out with a two month interval.

This study was undertaken to discover what initiates the transformation process and what happens in the crystal structure of salt X when the reaction occurs.

Experimental

A small crystal with approximate dimensions $0.25 \times 0.25 \times 0.20$ mm was used for X-ray structure analysis.

A test made on the intensities with a single-crystal diffractometer indicated Laue symmetry $\bar{3}$. Thus, possible space groups are $R3$ and $R\bar{3}$. The unit-cell dimensions were found to be $a = b = c = 18.225$ Å, $\alpha = \beta = \gamma = 30.515°$ ($a_h = 9.588$, $c_h = 51.959$) and $Z = 1$. Atomic absorption spectroscopy gives the ratio $K/Na = 1.17$, while the experimental density determined by means of flotation in heavy liquids is $\rho_o = 2.485$ Mg m^{-3}. These results will be compared with those of the structural analysis later.

Three-dimensional X-ray intensity data were collected on a Philips PW 1100 diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), the $\omega-2\theta$ scan mode, a scan width of $1.4°$ and a scan speed of $0.05°$ s^{-1}. A total of 2141 independent reflections were collected; the intensities were corrected for Lorentz and polarization factors, but not for absorption (owing to the very small dimensions of the crystal). 1607 reflections with $(I - 2\sqrt{I}) > B$ were used in the structure analysis. (I is the intensity in counts s^{-1} measured at the mean of two background measurements of 10 s each.) Three standard reflections were scanned throughout the data collection at intervals of every 200 reflections.

Determination and refinement of the structure

A piezoelectric test did not show the lack of a symmetry centre. Therefore, the crystal structure determination was carried out in space group $R\bar{3}$. However, in the final stage of refinement both space groups were tried, but the structure showed $R3$ to be the more reliable. The salt studied here was formed spontaneously through a solid-state reaction of salt X. The latter is characterized by $a = b \simeq 9.6$, $c \simeq 18$ Å and strong trigonal symmetry, so that the lattice parameters and symmetry are closely related to those of the compound which is now investigated. For these reasons it was supposed that the two salts were related both in chemistry and structure. Starting from the hypothesis that in both compounds there must be sandwich sheets of composition $[Na_2K_2Fe_6^{3+}O_2 (SO_4)_{12}(H_2O)_6]^{6-}$ and taking into account both c parameters and space groups, only two possible sequences of these sheets were derived, which probably included the correct crystal structure sequence; see Fig. 1 (Scordari, 1980b). On the other hand, the structures of metavoltine and salt X have been solved (Giacovazzo, Scordari, Todisco & Menchetti, 1976; Scordari, 1980a); in these the Fe^{3+} cation lies at $x \simeq 0.17, y \simeq 0.22$ or $x \simeq 0.22, y \simeq 0.17$. Other theoretical possibilities lead to sites equivalent to those just considered. These two sites together with the two
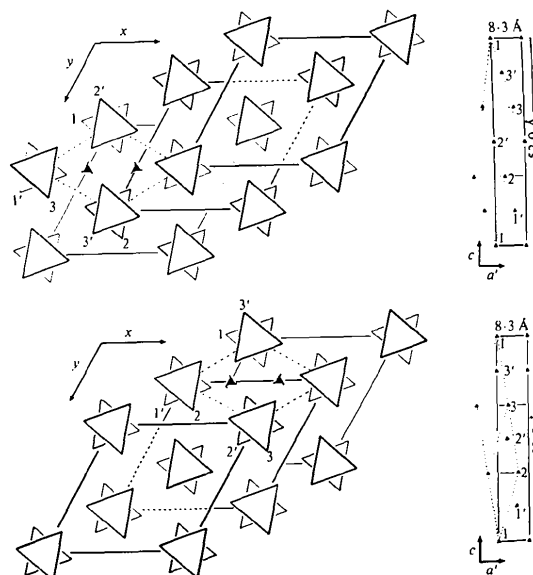

Fig. 1. The only two predicted ways (Scordari, 1980a) in which the structure of the crystal studied here can arrange sandwich sheets of composition $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}(H_2O)_6]^{6-}$.

Table 1. *Positional parameters and isotropic temperature factors of nonhydrogen atoms*

Standard deviations are in parentheses.

	x	y	z	B_{eq}/B (Å^2)
Fe	0.2458 (2)	0.1395 (2)	0.8652 (2)	1.4*
S(1)	0.3698 (3)	0.7978 (3)	0.9747 (3)	1.5*
S(2)	0.4342 (3)	0.8923 (3)	0.0566 (3)	1.5*
K(1)	0.2457 (1)	0.2457	0.2457	2.8*
K(2)	0.0	0.0	0.0	3.7*
Na	0.1723 (1)	0.1723	0.1723	2.0 (2)
O(1)	0.0869 (2)	0.0869	0.0869	1.4 (2)
O(2)	0.3936 (9)	0.9328 (9)	0.8722 (9)	2.4 (2)
O(3)	0.3905 (9)	0.0464 (9)	0.9186 (9)	2.1 (2)
O(4)	0.1594 (8)	0.3607 (8)	0.7997 (8)	1.6 (2)
O(5)	0.1390 (9)	0.2297 (9)	0.7907 (9)	2.2 (2)
O$_w$(6)	0.4367 (10)	0.2048 (10)	0.6172 (10)	2.9 (2)
O(7)	0.3897 (9)	0.2076 (8)	0.0107 (8)	2.0 (2)
O(8)	0.3696 (10)	0.9296 (10)	0.1538 (10)	2.5 (2)
O(9)	0.5198 (9)	0.6481 (9)	0.9870 (9)	2.4 (2)
O(10)	0.3324 (10)	0.8303 (10)	0.9021 (10)	2.8 (2)
P	0.3536 (8)	0.5068 (8)	0.7101 (8)	2.7 (2)
Q	0.3942 (14)	0.0650 (14)	0.5938 (14)	5.1 (3)

* Anisotropic thermal parameters for these atoms have been deposited. B_{eq} was calculated according to Hamilton (1959).

probable sequences shown in Fig. 1 give four probable solutions of the structure and all have been tested. However, three of these were excluded owing to the high R index (~ 0.60) for one Fe and two S atoms. After two cycles of full-matrix least-squares refinement, the most likely hypothesis gave an R value of 0.43.

Table 2. *Bond distances (Å), bond angles (°) and their estimated standard deviations for the title compound and, in square brackets, for salt X*

Fe—O(1)	1·92 (0)	[1·921 (2)]	O(1)—Fe[Fe(1)]—O(2)	97·9 (5)	[93·4 (4)]
Fe—O(2)	1·98 (2)	[2·014 (8)]	O(1)—Fe[Fe(1)]—O(3)	93·7 (5)	[97·0 (3)]
Fe—O(3)	2·00 (2)	[1·972 (8)]	O(1)—Fe[Fe(1)]—O(4)	96·7 (5)	[93·5 (4)]
Fe—O(4)	1·98 (1)	[2·005 (9)]	O(1)—Fe[Fe(1)]—O(5)	91·7 (5)	[97·7 (3)]
Fe—O(5)	2·03 (2)	[1·974 (9)]	O(1)—Fe[Fe(1)]—O$_w$(6)	178·4 (7)	[179·2 (3)]
Fe—O$_w$(6)	2·13 (2)	[2·135 (10)]	O(2)—Fe[Fe(1)]—O(3)	88·6 (7)	[89·2 (3)]
			O(2)—Fe[Fe(1)]—O(4)	165·4 (7)	[173·1 (5)]
S(1)—O(2)	1·50 (2)	[1·495 (10)]	O(2)—Fe[Fe(1)]—O(5)	88·3 (7)	[88·6 (3)]
S(1)—O(5)	1·49 (2)	[1·498 (10)]	O(2)—Fe[Fe(1)]—O$_w$(6)	83·6 (7)	[86·6 (4)]
S(1)—O(9)	1·46 (2)	[1·457 (12)]	O(3)—Fe[Fe(1)]—O(4)	90·6 (7)	[90·4 (3)]
S(1)—O(10)	1·44 (2)	[1·460 (10)]	O(3)—Fe[Fe(1)]—O(5)	174·1 (7)	[165·2 (4)]
			O(3)—Fe[Fe(1)]—O$_w$(6)	87·0 (7)	[82·1 (4)]
S(2)—O(3)	1·51 (2)	[1·509 (8)]	O(4)—Fe[Fe(1)]—O(5)	91·1 (6)	[90·0 (4)]
S(2)—O(4)	1·51 (2)	[1·496 (10)]	O(4)—Fe[Fe(1)]—O$_w$(6)	81·8 (7)	[86·5 (4)]
S(2)—O(7)	1·45 (2)	[1·455 (10)]	O(5)—Fe[Fe(1)]—O$_w$(6)	87·7 (7)	[83·1 (4)]
S(2)—O(8)	1·44 (2)	[1·441 (9)]			
			O(2)—S(1)—O(5)	108·0 (2)	[108·2 (5)]
K(1)[K]—O(7) × 3	2·88 (2)	[2·863 (9)]	O(2)—S(1)—O(9)	106·5 (1·0)	[110·2 (6)]
K(1)[K]—O(9) × 3	2·98 (2)	[2·905 (11)]	O(2)—S(1)—O(10)	110·2 (1·0)	[109·5 (6)]
K(2)—O(10) × 6	2·84 (1)		O(5)—S(1)—O(9)	110·5 (1·0)	[106·5 (6)]
			O(5)—S(1)—O(10)	109·0 (1·0)	[110·9 (6)]
Na—O(7) × 3	2·41 (2)	[2·425 (10)]	O(9)—S(1)—O(10)	112·5 (1·0)	[111·5 (6)]
Na—O(8) × 3	2·38 (2)	[2·380 (10)]			
			O(3)—S(2)—O(4)	106·9 (9)	[106·7 (5)]
P—P' × 2	2·99 (2)		O(3)—S(2)—O(7)	108·7 (9)	[107·3 (5)]
P—O(3)	2·86 (2)		O(3)—S(2)—O(8)	110·8 (1·0)	[109·9 (5)]
P—O(4)	3·14 (2)		O(4)—S(2)—O(7)	107·2 (9)	[109·4 (5)]
P—O$_w$(6)	2·98 (2)		O(4)—S(2)—O(8)	110·0 (1·0)	[110·4 (6)]
P—O(7)	2·96 (2)		O(7)—S(2)—O(8)	112·9 (1·0)	[112·8 (5)]
P—O(8)	3·07 (2)				
P—O'(8)	2·98 (2)				
Q—O(5)	3·04 (3)				
Q—O(10)	2·67 (3)				
Q—O'(10)	2·57 (3)				
Q—O(9)	2·54 (3)				
Q—Q'	2·77 (3)				

Subsequent Fourier syntheses revealed all the other non-hydrogen atoms. Another cycle of least-squares refinement with partial anisotropic thermal parameters reduced the R value to 0·079.

As in salt X, some problems arose in the refinement of this structure. There is a site fully filled by K and H_2O and, according to the occupancy coefficient $K:H_2O = 1:2$, this site as in salt X has been labelled P. Taking into account the chemical data ($K/Na = 1·17$), the electrostatic-balance calculation leads to an electrical charge difference of 0·7 cations per unit formula between the expected and found values. For this reason this defective positive charge has been assumed to be hydroxonium, extracted from the six structural waters.

Positional and thermal parameters are given in Table 1. Bond lengths and bond angles are in Table 2.*

Description and discussion of the structure

The main structural features of the compound are displayed in Figs. 2 and 3. To enable a comparison to be made between this structure and that of salt X from which it derives, the figures are shown in the hexagonal lattice and the sandwich sheet is rotated 60°. Therefore, to obtain all figures the following matrix must be applied to the atomic parameters quoted in Table 1:

$$\begin{vmatrix} \frac{1}{3} & \frac{1}{3} & \frac{\bar{2}}{3} \\ \frac{\bar{1}}{3} & \frac{2}{3} & \frac{\bar{1}}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{vmatrix}.$$

The most characteristic unit is a sandwich sheet of chemical composition $[Na_2K_2Fe^{3+}_6O_2(SO_4)_{12}(H_2O)_6]^{6-}$. Two subsequent sandwich sheets are rotated with respect to each other in such a way that one $[Fe^{3+}_3O(SO_4)_6(H_2O)_3]^{5-}$ cluster appears in front of the other at about 60° (Fig. 3). The distances found in the Fe octahedra are comparable with those of other similar salts; in particular, the much shorter Fe—O(1)
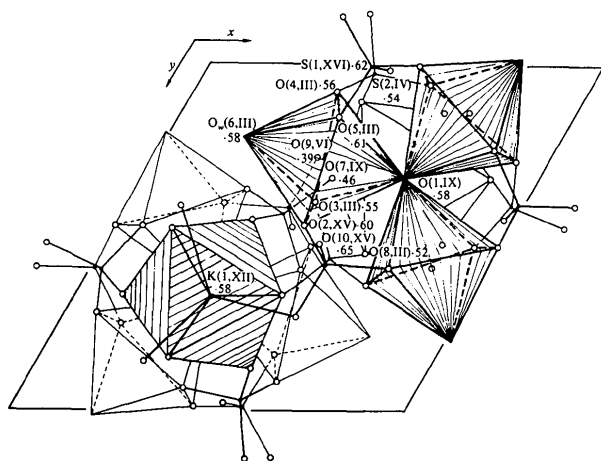
Fig. 2. The sandwich sheet of composition $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}$-$(H_2O)_6]^{6-}$ occurring in the present salt. Na and Fe octahedra are represented by hatched solids; the K polyhedron is clearly indicated.

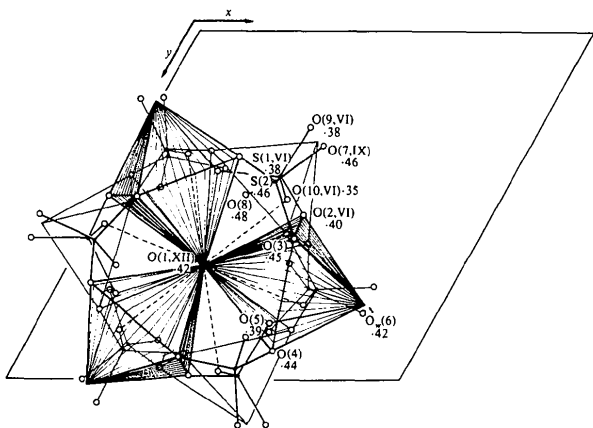Fig. 3. Two Fe^{3+} clusters belonging to two different sandwich sheets, one in front of the other and rotated by 60°. For clarity the centrosymmetrically related Fe^{3+} clusters have not been displayed.

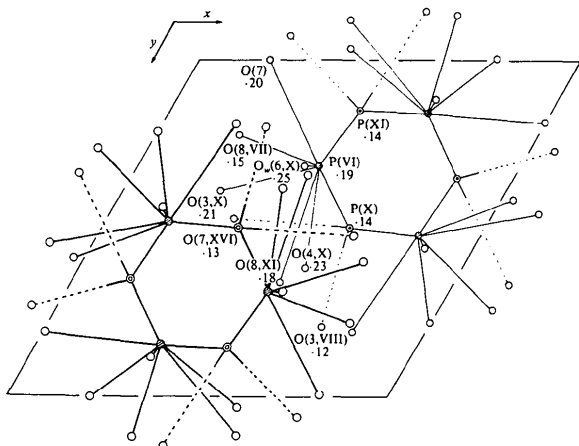Fig. 4. The crystal-chemical model built taking into account the ratio $K:H_2O = 1:2$. The sites around the triad axis are statistically filled by K and H_2O.
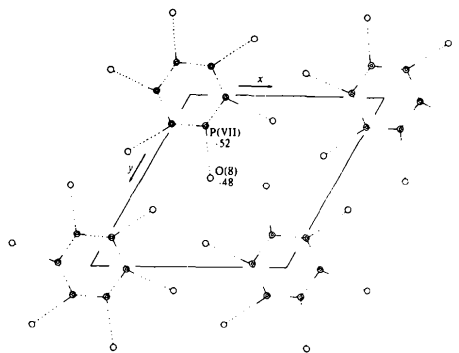
Fig. 5. This completes Fig. 4. Around the triad axis at (0·0, 0·0) there are only water molecules, in agreement with 3.

bond length (1·92 Å) and the longer $Fe-O_w(6)$ (2·13 Å) are present in α-Maus's salt (Giacovazzo, Scordari & Menchetti, 1975), metavoltine (Giacovazzo et al., 1976), salt X (Scordari, 1980a) and β-Maus's salt (Mereiter & Völlenkle, 1978). The same analysis may also be made for S—O distances in which there are two longer and two shorter ones (the former for oxygens shared by Fe^{3+} atoms) with mean values of 1·50 and 1·45 Å. As asserted above, the occupancy refinement leads to a ratio of $K:H_2O = 1:2$ (in Figs. 4 and 5 this site has been termed P).

A chemical analysis confined to potassium and sodium atoms indicates that in the unit formula there are 5 K and 4·28 Na. Structural and chemical results concord and allow the following crystal-chemical formula: $K_3(K_{0.333},H_2O_{0.667})_6Na_2(Na_{0.38},H_3O_{0.12}^+$-$H_2O_{0.50})_6Fe_6^{3+}O_2(SO_4)_{12}.6H_2O$. Also, the density calculated from this formula is very similar to that measured: $\rho_o = 2·485$, $\rho_c = 2·482$ Mg m^{-3}.

The structure of our compound is closely related to the structure of metavoltine, salt X and α-Maus's salt. In fact, like the former two salts it has a sandwich sheet of chemical composition $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}$-$(H_2O)_6]^{6-}$ (Fig. 2). As in α-Maus's salt the Fe^{3+} clusters, belonging to two $[KFe_3^{3+}O(SO_4)_6(H_2O)_3]^{4-}$ sheets at about 9 Å, are in front of one another, rotated by 60° and interconnected via K atoms.

Hydrogen bonds

The hydrogen bonds shown in Figs. 4, 5 and 6 meet electrostatic and geometrical requirements. Table 3 has been calculated taking into account the bond-strength–bond-length curves given by Brown & Shannon (1973), while Baur's (1972) criteria and Ferraris & Franchini-Angela's (1972) suggestions have been kept in mind when the oxygens were selected for the proposed hydrogen-bond system. The universal bond-strength–bond-length curve has been used for H_3O^+ instead of the individual ones employed for all other atoms.

Table 3. *Electrostatic valence balance in the compound investigated*

	Fe	S	K	Na	P_K	$Q_{H,O}$	H—		···H	Sum
O(1)	0.620 (×6)									3.720
O(2)	0.530 (×6)	1.383 (×6)[a]							0.12 (×3)	11.838
O(3)	0.497 (×6)	1.375 (×6)[b]			0.155 (×2)				0.17 (×2)	11.882
O(4)	0.530 (×6)	1.385 (×6)[b]			0.098 (×2)				0.13 (×6)	12.466
O(5)	0.467 (×6)	1.409 (×6)[a]							0.16 (×3)	12.087
O_w(6)	0.356 (×6)				0.129 (×2)		{ 0.87 (×6) 0.81 (×6)			12.474
O(7)		1.591 (×6)[b]	0.180 (×6×3)[a]	0.1617 (×6×3)	0.132 (×2)				0.15 (×2)	16.261
O(8)		1.649 (×6)[b]		0.1717 (×6×3)						
O(9)		1.562 (×6)[a]	0.1528 (×6×3)[a]		{ 0.109 (×2) 0.128 (×2)	0.255 (×3)			0.15 (×2)	14.523
O(10)		1.646 (×6)[a]	0.167 (×6×6)[b]						0.19 (×6)	13.262
$P_{H,O}$							{ 0.206 (×3) 0.245 (×3)			17.241
$Q_{H,O}$					0.125 (×2×2)		{ 0.85 (×2) 0.83 (×2)	{ 0.85 (×2) 0.85 (×2)	0.15 (×2)	7.560
						0.177 (×3)	{ 0.88 (×3) 0.84 (×3)			5.691
Sum	18.00	72.00	12.00	6.00	2.00	3.00	22.00		4.00	139.00

(a) indicates S(1), K(1), and (b) S(2), K(2).
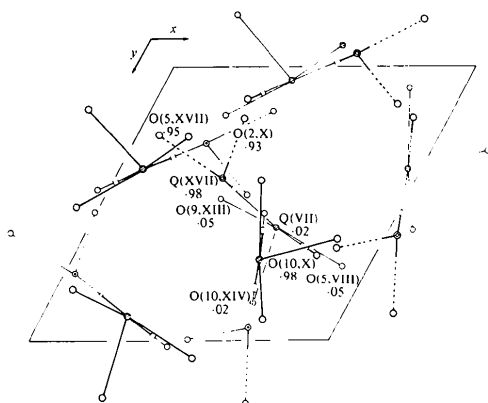
Fig. 6. The model drawn according to the hypothesis that Na, H_3O^+ and H_2O statistically fill the site indicated by Q.
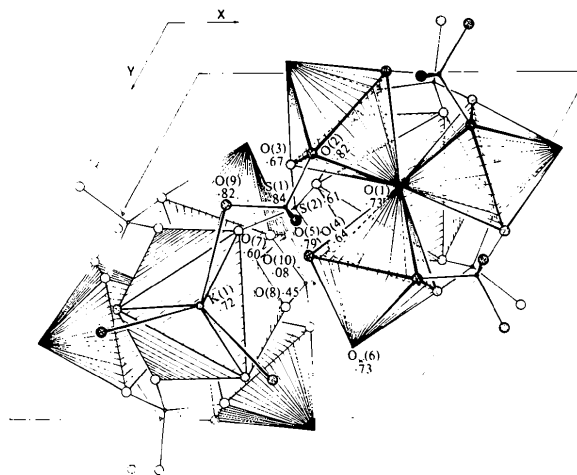
Fig. 7. The sandwich sheet present in salt X has the same composition as that shown in Fig. 2. Note the different orientations of the Fe^{3+} clusters.
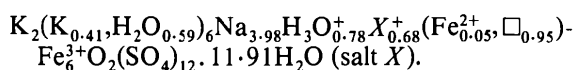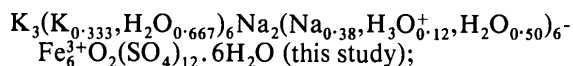
Comparison between salt X and its topotactic product

In Table 2 the bond lengths and bond angles of the polyhedra forming the $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}(H_2O)_6]^{6-}$ sandwich sheet in salt X are quoted in square brackets. In Table 2 the same symbolism is used for the title compound and salt X; therefore, it is possible to compare distances and angles to understand what happens in the structure of salt X when the solid-state reaction has taken place. We can see that except for Fe—O(1) and Fe—O_w(6), the other Fe—O distances are changed in such a way that Fe—O(2) of our compound is approximately equal to Fe—O(3) of salt X and *vice versa*; the same is true for Fe—O(4) and Fe—O(5). Differences can also be found in the angles. As for SO_4 tetrahedra there are hardly any traces of disagreement between the distances of the two compounds, but there are for O—S—O angles. These differences can be ascribed to the rotation of about 25° that the $[Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{5-}$ cluster undergoes when salt X transforms into the salt investigated here. From a comparison of Figs. 2 and 7 it can be seen that the Fe^{3+} clusters are differently oriented in the two structures with a consistent rotation of Fe octahedra along the O(1)—Fe—O_w(6) direction.

Salt X has been obtained at about 353 K and slowly changes into our compound when in contact with the mother liquor at room temperature. From the analysis of the salt X structure compared to that of our compound a more accentuated disorder for the former salt ensues. In particular, this disorder concerns one half of the Na atoms. The sandwich sheet of composition $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}(H_2O)_6]^{6-}$ is a stable configuration present in both salts. The crucial point is the connection between two such sandwich sheets that in salt X mostly occurs through disordered Na atoms. Still, in this salt Na atoms are connected to seven oxygens of which three are always O(10) belonging to the sandwich sheet and shared S(1) and Na. When the ordering process starts, Na releases this oxygen and another configuration with chemically unchanged sandwich sheets arises. Therefore, in this reaction, as

expected, only weak chemical bonds are broken. Moreover, the geometry of the reactant lattice determines this solid–solid reaction through a translation of the sandwich sheets equal to $\frac{1}{3}$ of the long diagonal of the hexagonal net (Fig. 1).

It is useful to compare also the two crystal-chemical formulae of the compounds before and after the topotactic reaction:

$$K_3(K_{0.333},H_2O_{0.667})_6Na_2(Na_{0.38},H_3O^+_{0.12},H_2O_{0.50})_6\text{-}$$
$$Fe_6^{3+}O_2(SO_4)_{12}.6H_2O \text{ (this study);}$$

$$K_2(K_{0.41},H_2O_{0.59})_6Na_{3.98}H_3O^+_{0.78}X^+_{0.68}(Fe^{2+}_{0.05},\square_{0.95})\text{-}$$
$$Fe_6^{3+}O_2(SO_4)_{12}.11.91H_2O \text{ (salt } X).$$

From a comparison of the two formulae we can see a general disagreement concerning cations and water molecules. Unfortunately, there are objective limits in the crystal-chemical formula of salt X. This formula has been determined only through structural analysis; moreover, there are some atoms labelled X^+ not directly found in the unit cell. We met with serious difficulties when we tried to measure the K/Na ratio and the density of salt X, since about two months later this salt unexpectedly changed into the compound studied here. Also, attempts made to obtain salt X again were unsuccessful. In fact, very slight fluctuations in temperature and in the concentration of the salts used for crystallization seem to produce crystals with a different K/Na content. Thus, the following K/Na ratios have been observed in other crystallizations: 0.27, 0.34, 0.47, 0.65. However, other K/Na ratios are also possible; for instance, on changing the $Na_2SO_4.10H_2O$ and K_2SO_4 concentration a compound with K/Na = 10.75 has been obtained. Moreover, with similar physicochemical conditions a salt with $c \simeq 36$ Å has been obtained (Scordari, 1977a, 1980c) and an unstable K/Na Maus's salt which changes into ferrinatrite (Scordari, 1977b). Finally, salt X frequently shows merohedric twinning (Scordari, 1980a), further complicating the K, Na determination in these salts.

Nevertheless, some general remarks can be inferred. We note quite a similar hydroxonium and alkaline content in salt X and in its product. In addition, we observe that the topotactic reaction of salt X is probably the response to changes in temperature (from 353 K to room temperature) of the crystal examined here. Consequently, corresponding to a random distribution of Na and to a greater coordination number for Na polyhedra (sevenfold), at room temperature we have another structure in which these cations are less disordered and more firmly linked to the surrounding oxygens (fivefold coordinated). These quite different Na coordination numbers seem to be the main reason for a shortering of the c parameter; in fact, $\frac{1}{3}c_h$ (17.32 Å) found for the topotactic product is smaller than c of salt X (18.02 Å).

The thickness of the sheet $[Na_2K_2Fe_6^{3+}(SO_4)_{12}\text{-}(H_2O)_6]^{6-}$ in both structures is the same (8.2 Å); in contrast, the intersheet distance is 9.1 Å in salt X and 8.3 Å in its product.

Finally, in agreement with Oswald & Günter (1979) this transformation may be classified as a two-dimensional topotactic reaction with loss of water.

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