Structural considerations of some natural and artificial alkali iron hydrated sulphates[1]

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SYNOPSIS

TWO compounds are described which are structurally related to the three salts, metavoltine, α-Maus' salt, and an unnamed compound here termed 'salt X'. The last three salts have structures based on two sheets of composition $[K\ Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{4-}$ which are essentially interconnected via Na atoms in metavoltine, K-atoms in α-Maus' salt and Na, K, H_3O in salt X.

Cell parameters and space groups of the new compounds have been determined: as in metavoltine, α-Maus' salt, and salt X they have $a = b \simeq 9.6$ Å, but the c parameters are $\simeq 36$ Å and $\simeq 52$ Å, i.e. about double and triple that of the other three salts ($\simeq 18$ Å).

The salt with $c \simeq 36$ Å was obtained using Van Tassel's recipe at about the same conditions which gave rise to salt X, i.e. from a solution containing $Na_2SO_4 \cdot 10H_2O$, K_2SO_4, $Fe_2(SO_4)_3 \cdot nH_2O$ (n $\simeq$ 7H$_2$O) in the ratio 3.40:0.60:4.30. The salt with $c \simeq 52$ Å was formed spontaneously through a topotactic reaction of salt X.

It is possible to deduce for these two new salts:

(1) The presence of clusters of composition $[Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{5-}$ interconnected via K atoms to build sheets like those found in metavoltine, α-Maus' salt, and salt X.

(2) Some sheet sequences which may include the correct sequence.

(3) The position of Fe^{3+} atoms belonging to clusters, which are connected by K atoms to form sheets.

The similar a and b lattice parameters, as well as the presence of the threefold axis in all the compounds mentioned, suggest strongly that in the two new compounds there are sheets of composition $[K\ Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{4-}$ which are characterized by $a = b \simeq 9.6$ Å and threefold symmetry. As for the c parameters, examination of possible stacking sequences of the sheets shows which sequences are consistent with the known c parameters and symmetry. The two salts have a parameter and symmetry more similar to metavoltine and salt X than to α-Maus' salt; moreover, metavoltine and salt X, like the new salts, are more stable than α-Maus' salt. That is why probably in the two new salts there are two sheets interconnected by Na atoms as in metavoltine and salt X to form a sandwich sheet of composition $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}(H_2O)_6]^{6-}$. Then, taking into account the c parameters and space groups, possible sequences of these sandwich sheets are considered in order to establish the likely sequence in the new salts.

Metavoltine and salt X contain clusters $[Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{5-}$ which are differently oriented: the Fe^{3+} cation lies at $x = 0.17$, $y = 0.22$ or $x = 0.22$, $y = 0.17$. These two Fe^{3+} positions involve an angle rotation for the cluster of about 25°. Owing to the similarity in a, b parameters of metavoltine and the salt with $c \simeq 52$ Å on one hand, and of salt X and the salt with $c \simeq 36$ Å on the other, it seems quite probable that the xy coordinates of the Fe^{3+} cations belonging to the first pair of salts are similar, and similarly for the second pair.

(Na, K) α-Maus' salt effloresces in air, the products being ferrinatrite and goldichite. The transformation (Na, K) α-Maus' salt→ferrinatrite was clarified when the structure of ferrinatrite was solved. The transition (Na, K) α-Maus' salt→goldichite is considered in order to understand how $[Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{5-}$ clusters may be modified to build new structural units such as the corrugated sheets present in goldichite.

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STRUCTURAL CONSIDERATIONS OF SOME NATURAL AND
ARTIFICIAL ALKALI IRON HYDRATED SULPHATES

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Recent papers have described certain alkali iron hydrated
sulphates which are inter-related in both chemistry and structu
re (Scordari et al., 1975; Giacovazzo et al., 1975; Giacovazzo
et al., 1976; Scordari, 1977a; Scordari, in preparation). In the
present work some crystal chemical questions concerning the stru
ctural organization of these sulphates are reconsidered and after
wards, on this basis, some considerations are made on the atomic
arrangement of two new compounds related to them. The structure
solution of ferrinatrite, $Na_3(H_2O)_3Fe(SO_4)_3$ (Scordari, 1977b) al
lowed an understanding of the relationship between ferrinatrite
and (Na, K) a-Maus' salt, $K_2(K_{0.5-x}, Na_x, H_2O_{0.5})_6Fe^{3+}_3O(SO_4)_6 \cdot$
$7 H_2O$ where $0 \leqslant x < 0.34$ (Scordari, in preparation) from which it
derives. However, when (Na, K) a-Maus' salt effloresces it also
produces goldichite, $K Fe(SO_4)_2 \cdot 4H_2O$ which, at first sight seems
to have a very different structure. Now it is possible to show
the structural implications involved in the (Na, K) a-Maus' salt
$\rightarrow$goldichite transformation. We start from the Fe-O-S units pre
sent in a-Maus' salt (Giacovazzo et al., 1975) and by a suitable
combination of them we derive other possible arrangements. The
symbolism of Moore and Araki (1974) is used to describe the to-
pology of the structures discussed here.

Considerations on two sulphates with unknown structures. The
cluster with chemical composition $[Fe^{3+}_3O(SO_4)_6(H_2O)_3]^{5-}$ is a
configuration encountered in several structures (Giacovazzo et
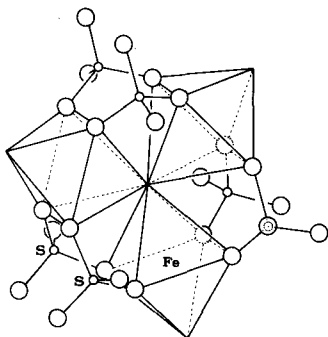al., 1975; Giacovazzo et al., 1976; Mereiter und Vollënkle, 1978;

Fig. 1   Cluster of composition $[Fe^{3+}_3O(SO_4)_6(H_2O)_3]^{5-}$ present
in some alkaline iron hydrated sulphates.

Scordari, in preparation). This cluster is made up of three Fe^{3+}
octahedra sharing a vertex and six SO_4 tetrahedra (fig.1). Ex
cept for β-Maus' salt (Mereiter und Vollënkle, 1978), the stru
ctures which contain this cluster, namely metavoltine, $K_2Na_6Fe^{3+}_6$
$(SO_4)_{12}O_2 \cdot 18H_2O$ (simplified formula), a-Maus' salt and another
synthetic salt, $K_2(K_{0.41}, H_2O_{0.59})_6Na_{3.98}H_3O_{0.78}X^+_{0.68}(Fe^{2+}_{0.05}, \square_{0.95})$
$Fe^{3+}_6O_2(SO_4)_{12} \cdot 15.39 H_2O$ (Scordari, in preparation; from now on
termed "salt X") have comparable symmetries and lattice constants.
Two compounds have been obtained which have approximately double
or triple c parameters, compared with those of metavoltine, a -
Maus' salt and salt X. The former with $c \simeq 36$ Å, was obtained
following Van Tassel's recipe (Van Tassel, 1961; Scordari, 1977a);
the latter, with $c \simeq 52$ Å, is the topotatic transformarion of
salt X. Starting from the information obtainable from the re-
solved structures (metavoltine, a-Maus' salt, salt X), an attempt

has been made to deduce the structural relationship between the
clusters in these two new compounds. In order to achieve this,
it is useful to examine the cluster more closely. The $[Fe^{3+}_3O$
$(SO_4)_6(H_2O)_3]^{5-}$ unit has a residual negative charge, that may
be placed on the oxygen atoms, belonging to SO_4 groups and not
shared by Fe^{3+} cations. The electrostatic repulsive forces bet
ween two such units are minimized if the following conditions
are observed:

1) Two adjacent clusters, lying in the xy plane, have the same
   orientation with the Fe-octahedron vertex pointed at SO_4 te
   trahedra.

2) If along the c axis there are opposite clusters separated by
   about 9 Å, they are rotated one with regard to the other by
   60°.

Moreover the cluster has about the same dimensions in the
xy plane and perpendicular to it; two of these clusters are con
nected to each other by K or Na polyhedra, both about the same
size. These facts, together with the two conditions given above,
involve the $c \simeq 2a$ relation. Clusters are interconnected by K
atoms to form layers in the xy plane. If some cluster layers
are shifted in the xy plane, in general $c \simeq 2n \cdot a$ (where n has the
observed values 1, 2, 3). Owing to the electrostatic repulsion
the clusters must be as far away as possible from each other.
The result of this is that those S-O bonds no longer engaged in
the cluster tend in part to lie in the xy plane and in part
perpendicular to the xy plane. From two resolved structures
(metavoltine and salt X) we may deduce two possibilities: the
Fe^{3+} cation is either at $x \simeq 0.17$ and $y \simeq 0.22$ or at $x \simeq 0.22$ and
$y \simeq 0.17$. This caused two possible orientations of the cluster
with an angle difference of about 25° (Scordari, in preparation).
Considering the Fe^{3+} positions given above, other orientations
which involve an angle difference of 60° from the starting po
sitions lead back to the starting-point. Three structures ha
ve been solved which are closely related to the unknown ones
of the two compounds investigated here. The lattice parameters
and space groups are respectively:

a = 9.71   c = 18.96 Å   P6_3/m a-Maus' salt(Giacovazzo
                                                  et al., 1975)
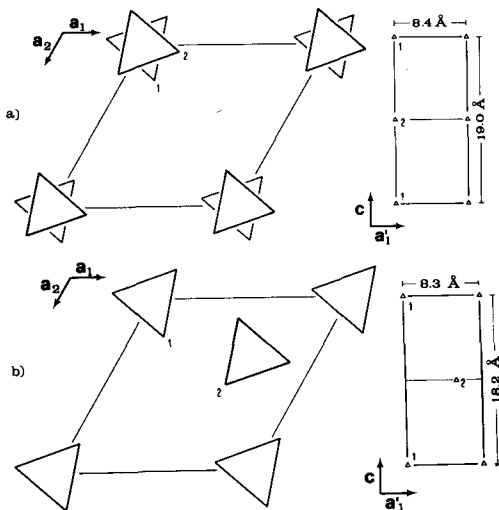
Fig. 2   Triangles indicate $[Fe^{3+}_3O(SO_4)_6(H_2O)_3]^{5-}$ clusters.
a) Schematic representation of a-Maus' salt.
b) Schematic representation of metavoltine and salt X.

a = 9.575   c = 18.17 Å   P3   metavoltine (Giacovazzo et al., 1976)

a = 9.643   c = 18.018 Å   P1 (pseudo P3)   "salt X" (Scordari, in preparation)

a = 9.642   c = 35.93 Å   P$\bar{6}$2c or P6$_3$mc or P6$_3$/mmc   unknown structure

a = 9.588   c = 51.958 Å   R$\bar{3}$ or R3   unknown structure

Describing the cluster shown in fig.1 by means of an equilateral triangle we have for α-Maus' salt on one hand and for metavoltine and salt X on the other, the schemes displayed in figs. 2a and 2b. Now, unlike the second cluster arrangement (fig. 2b), the first leads to compounds which are unstable at standard conditions. The two salts with unknown structures are stable in air and have a parameters similar to those of salt X or metavoltine. For both these reasons they probably have a structure based on a double layer of composition [Na$_2$K$_2$Fe$^{3+}_6$O$_2$(SO$_4$)$_{12}$ (H$_2$O)$_6$]$^{6-}$ like that shown in fig. 3 and outlined in fig. 2b, which from now on we call a sandwich sheet. It is possible to say something about the unknown structures rebuilding the stacking sequence of the sandwich sheet on the basis of the space group and the c lattice parameters of the new salts. For two or three layer periodicities, there are respectively two simple stacking sequences of the hexagonal or rombohedral lattice. In the structure of salt with c ≃ 36 Å and in that of salt with c ≃ 52 Å there are four and six layers of composition [K Fe$^{3+}_3$O(SO$_4$)$_6$ (H$_2$O)$_3$]$^{4-}$ respectively. Owing to the constrains between two such layers (always interconnected by Na atoms as shown in fig. 3) we may reduce the number of these simple layers from four or six to two or three sandwich sheets like those shown in fig. 3.

But there are other possibilities that must be considered; in fact between two sandwich sheets there is in salt X and metavoltine a cation layer which allows several theoretical con
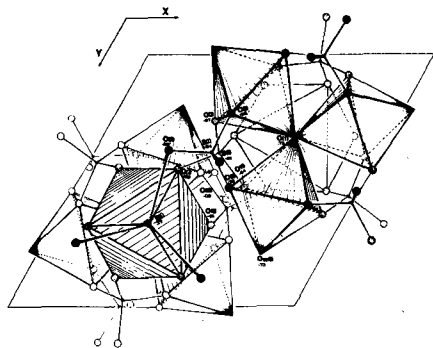
five, two are less favoured because of the second condition quoted above. The five cases are illustrated in fig. 4 and correspond to a translation (1/3, 2/3), to a rotation around the short diagonal of the net combined with a translation (2/3, 1/3), to a rotation around the long diagonal of the net accompanied by a translation (1/3, 2/3), and, finally, to two pure rotations around the short and the long diagonals of the net respectively.
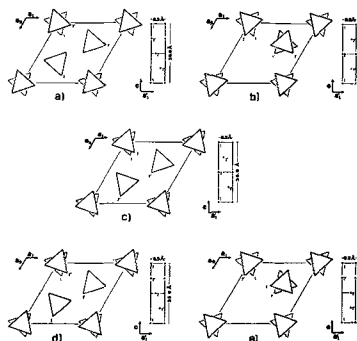

Fig. 4   Possible schemes of part of the structure of the salt with c ≃ 36 Å. Arrangements shown in a, b, c, are more likely than those shown in d, and e.
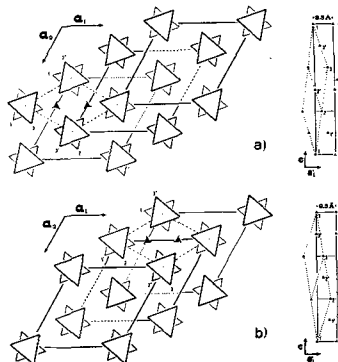

Fig. 5   The only two ways in which the structures of the crystal with c ≃ 52 Å may arrange its iron clusters. The R lattice proved to be very restrictive in reducing the possible dispositions.

Fig. 3   A sandwich sheet with composition [Na$_2$K$_2$Fe$^{3+}_6$O$_2$(H$_2$O)$_6$ (SO$_4$)$_{12}$]$^{6-}$. Na and Fe octahedra are represented by hatched solids. Three Fe-octahedra sharing a vertex are connected by means of six SO$_4$ groups. Na atoms (not shown in fig.) are on the triad axes at 1/3, 2/3 and 2/3, 1/3 forming distorted octahedra. K atoms (shown in fig.) are on the same threefold axes forming distorted prisms, which share faces with Na-octahedra.

nections between two sandwich sheets. It may be the three possible space groups mentioned above do not describe the correct symmetry of the crystal (c ≃ 36 Å). Let us consider two sandwich sheets and the possible translations, rotations and rototranslations of one of these sheets in relation to the other. Fixing the Fe^{3+} cation position according to x and y already given for the first compound (c ≃ 36 Å, hexagonal lattice) we obtain eight possibilities of which three are identical and, of the remaining

Taking into account the second salt and in accordance with the rombohedral primitive lattice (R$\bar{3}$ or R3) and c ≃ 52 Å, only two translations for the sandwich sheet are possible. The first (1/3, 2/3) corresponds to the obverse setting and the second (2/3, 1/3) to the reverse setting of an R-lattice. The result of this operation is sketched in fig. 5 and shows two possible cluster sequences in the rombohedral cell for this last compound. In figs. 2b, 3, 4, and 5, the clusters are numered according to increasing z coordinates.

Structural relationship between (Na, K) α-Maus' salt and goldichite. Na-enriched α-Maus' salt effloresces in air, breaking down into ferrinatrite and goldichite (Scordari, 1977a). The structures of these two compounds are known (Scordari, 1977b; Graeber and Rosenzweig, 1971), so it is interesting to consider what happens when the transformation occurs. The cluster with chemical composition [Fe$^{3+}_3$O(SO$_4$)$_6$(H$_2$O)$_3$]$^{5-}$ may be transformed

into two other units with different topologies but with the same chemical composition (fig. 6). Let us define as the "basic unit" the first cluster and as "derivative units" the other two clusters obtained from the first one. The basic unit is present in some stable and unstable structures at standard conditions (see above). The first derivative unit (fig. 6a), is a self-consistent unit and this is present in the structures of coquimbite, $(Fe^{3+}, Al)_2(SO_4)_3 \cdot 9H_2O$, and paracoquimbite (Fang and Robinson, 1970; Giacovazzo, et al., 1970; Robinson and Fang,

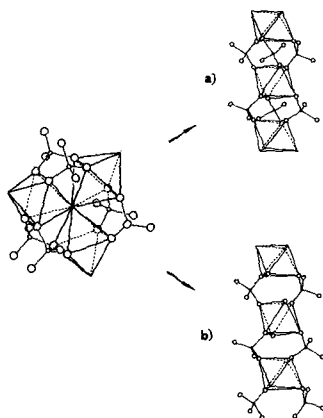can polymerize with the contribution of three additional SO_4 groups to build a different Fe-O-S chain shown in fig. 7a. Bond chains arising from the first derivative unit (fig. 6a) have been found in ferrinatrite (Scordari, 1977b) where the network relationship between this mineral and α-Maus' salt (Na, K) are also shown, while corrugated sheets of Fe-octahedra and SO_4 tetrahedra arising from the second derivative unit (fig. 6b) are present in goldichite. Fig. 8 shows four goldichite cells, without any water molecules and K atoms, projected along the a axis (Graeber and Rosenzweig, 1971). It is useful to compare this structure with the corrugated sheet of octahedra and tetrahedra drawn in fig. 7b. Finally in fig. 9 the lattice connections between goldichite and (Na, K) α-Maus' salt are shown. Goldichite is monoclinic with space group $P2_1/c$ and cell parameters: $a = 10.387$, $b = 10.486$, $c = 9.086$ Å, $\beta = 101.7°$; the crystal data of α-Maus' salt are quoted above. The triangles at the vertex of the two—

Fig. 6 $[Fe_3^{3+}O(SO_4)_6(H_2O)_3]^{5-}$ cluster composition, which convert to structural units with the same chemical composition but different topology.

Fig. 8   Crystal structure of goldichite; four cells seen along a axis without K atoms and structural water.
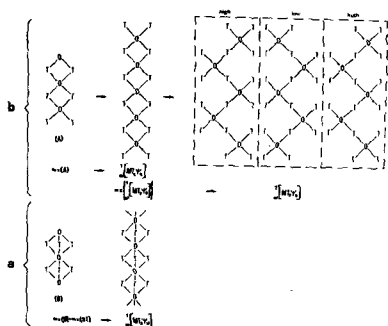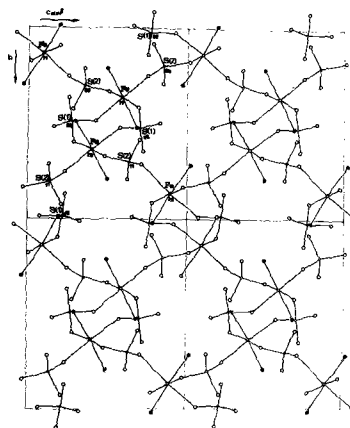

Fig. 7   The two derivative units of fig. 6 represented by O (octahedra) ant T (tetrahedra). A represents structure (b) in fig. 6 and B represents structure (a). They polymerize to form Fe-O-S bond chains as in ferrinatrite and Fe-O-S bonds sheets as in goldichite. High and low indicate atoms which have x-coordinates positive and negative respectively as to the drawing sheet, so this representation describes the corrugated sheets as are formed in goldichite.
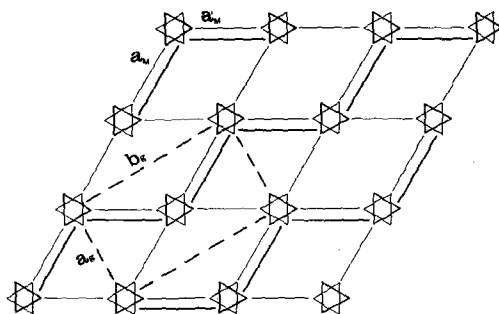

Fig. 9   Relationship between α-Maus' salt (full lines) and goldichite network (dashed lines). Dark full lines represent Fe-O-S corrugated sheets.

1971). The second derivative unit (fig. 6b) is not self-consistent and needs other similar units to make a chain of Fe-O-S bonds (fig. 7b). A successive polymerization step of the second derivative unit leads to the interaction of Fe-O-S chains to generate a corrugated sheet of $Fe(0)_5H_2O$ octahedra and SO_4 tetrahedra (see fig. 7b). On the other hand, the first derivative unit (fig. 6a), too,

dimensional lattice are iron-clusters which evolve according to fig. 7b, to build the corrugated sheets of octahedra and tetrahedra present in goldichite (dark full lines): a_M is the lattice parameter of α-Maus' salt, while a_g and b_g are those of goldichite

chite. These latter parameters are respectively along the short and the long diagonal of the a-Maus' salt unit cell. The long diagonal, which measures 16.82 Å, shortens in goldichite owing to a direct interaction between the clusters, while c_g (goldichite) is about half a_M (a-Maus' salt), that is about the length of the cluster represented in fig. 6a. As regards the β angle of goldichite, we observe that the K atoms are in the sheets to reinforce their cohesion while the structural water is between them to connect them one to another, producing a shift which alters the theoretical angle value of 90°. According to the symbolism of Moore and Araki (1974) and assuming half of the tetrahedral oxygens are bonded to one M (Fe^{3+}) and one T (S^{6+}) in goldichite as in ferrinatrite, the stoichiometries $MT_2\psi_8$ and $MT_3\psi_{12}$ have important topological properties i.e. indefinitely extending layers and chains of octahedra and tetrahedra respectively. This advantageous symbolism is used to synthesize the polymerizations illustrated in fig. 7.

Conclusions. An analysis of the possible stacking sequences based on a sandwich sheet of composition $[Na_2K_2Fe_6^{3+}O_2(SO_4)_{12}(H_2O)_6]^{6-}$ has yielded several interesting sequences which may include the correct sequence and the oxy Fe^{3+} coordinates in the two salts. So the compound with the hexagonal lattice and $c \simeq 36$ Å may show five stacking sequences, of which three are favoured; while as to the compound with the rombohedral lattice and $c \simeq 52$ Å, the conditions are more rigorous than in the first case allowing only two possible sequences. One of two possible transformations that occur when (Na, K) a-Maus' salt dehydrates, has already been explained. Here, starting from the basic unit the change involving goldichite is clarified. In fact, by successive polymerizations of this unit we are able to build corrugated sheets of Fe-O-S bonds as are found in goldichite.

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