# Structure and Twinning in $\left(\mathrm{Na}_{0.12}, \mathrm{H}_{3} \mathrm{O}^{+}{ }_{0.38}, \mathrm{H}_{2} \mathrm{O}_{0.50}\right)_{6}\left(\mathrm{Na}_{0.12}, \mathrm{H}_{3} \mathrm{O}^{+}{ }_{0.88}\right)\left[\mathrm{K}_{2}\left(\mathrm{~K}_{0.333}, \mathrm{H}_{2} \mathrm{O}_{0.667}\right)_{6}-\right.$ $\left.\mathrm{Na}_{\mathbf{2}} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{\mathbf{2}}\left(\mathbf{S O}_{4}\right)_{12} \cdot \mathbf{6} \mathrm{H}_{2} \mathrm{O}\right]$ 

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#### Abstract

Na}_{2} \cdot 84 \mathrm{~K}_{4}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)_{3.16} \mathrm{Fe}_{6} \mathrm{~S}_{12} \mathrm{O}_{50} .13 \mathrm{H}_{2} \mathrm{O}, \quad M_{r}=\) 2035.83, $P \overline{3} 1 c, a=b=9.620$ (6), $c=35.971$ (8) Å, $V=2882.92 \AA^{3}, \quad Z=2, \quad D_{m}=2.35 \quad$ (by flotation), $D_{x}=2.34 \mathrm{Mg} \mathrm{m}^{-3}, \quad$ Мо $K \alpha, \quad \lambda=0.7107 \AA, \quad \mu=$ $2.66 \mathrm{~mm}^{-1}, F(000)=1020, T=290 \mathrm{~K}$, final $R=0.12$ for 462 observed reflections. Suitable crystals for this study were prepared from an aqueous solution containing sodium, potassium and iron sulphates at about 350 K . The structure solution confirmed the hypothesis that the crystal investigated was really a merohedric twin. The percentages found for the two individuals are 48 and $52 \%$ respectively. The most important structural units are sandwich sheets of composition $\left[\mathrm{Na}_{2} \mathrm{~K}_{2} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{6-}$ (simplified formula), which have previously been found in other similar compounds.


Introduction. This paper is part of a series of investigations of some sulphates containing the same $\mathrm{Fe}^{3+}$ trinuclear complex (Giacovazzo, Scordari \& Menchetti, 1975; Giacovazzo, Scordari, Todisco \& Menchetti, 1976; Scordari, 1980a, 1981). The analysis of the title compound presented some difficulties. Crystals from the same batch showed changeable $\mathrm{Na} / \mathrm{K}$ ratio (Scordari, 1977). Moreover, all the crystals examined by Weissenberg photographs indicated a symmetry higher than expected. Finally, X-ray powder patterns proved that the $\left(\mathrm{K}, \mathrm{H}_{3} \mathrm{O}^{+}\right)$-rich crystals were more stable than the Na -rich ones. The reasons for undertaking this structural analysis are: (a) to determine the sites involved in the $\mathrm{Na}, \mathrm{K}$ and $\mathrm{H}_{3} \mathrm{O}^{+}$replacement; (b) to understand the reasons which make the Na -enriched compounds unstable; (c) to examine the relationships between the title compound and other closely related salts (Scordari, 1980a, 1981); (d) to verify the correct stacking sequence of $\left[\mathrm{Na}_{2} \mathrm{~K}_{2} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{16-}\right.$ double sheets (Scordari, 1980b); and (e) to prove that the unusual symmetry exhibited by the compound was due to a twinning effect.

Experimental. Title compound grows at about 350 K by evaporation of an aqueous solution containing $\mathrm{K}_{2} \mathrm{SO}_{4} \quad(0.6 \mathrm{~g}), \quad \mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O} \quad(3.4 \mathrm{~g}) \quad$ and

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$\mathrm{Fe}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot n \mathrm{H}_{2} \mathrm{O}(4 \cdot 3 \mathrm{~g})$. The crystals obtained usually effloresce slowly; however, the crystal analysed was stable and hexagonal with approximate dimensions $0.014 \times 0.014 \times 0.016 \mathrm{~cm} . \quad D_{m}$ was determined by flotation with the same crystal used for the X-ray analysis. Philips PW 1100, graphite-monochromated Mo $K \alpha, \omega-2 \theta$ scan mode, three standard reflections $(11,1,0,0,0,18$ and $\overline{12}, 1,0)$ measured every 100 reflections showed no significant changes. 10 reflections in the range $7^{\circ}<\theta<13^{\circ}$ were used for measuring lattice parameters; no absorption correction $\left(\mu R_{\max }=0.43\right)$. Scattering curves from Cromer \& Waber (1965). Within a range of $(\sin \theta) / \lambda<0.50 \AA^{-1}$, 864 reflections with $\left|F_{o}\right|>3 \sigma\left(F_{o}\right)$ were selected from a total of 1491 measured; $h_{\text {max }}=k_{\text {max }}=8$ and $l_{\text {max }}=36$.
A piezoelectric test did not confirm the lack of a centre of symmetry.
Problems concerning a symmetry higher ( $\mathrm{P} 6 / \mathrm{mmm}$ ) than the structure allowed were overcome by assuming that the crystal was a [11 $\overline{2} 0]$ twin. $P \overline{3} 1 c$ proved to be more reliable than $P \overline{6} 2 c$ for the structure solution. Were the crystal a merohedric twin, the pairs of reflections $h k l$ and $k h \bar{l}$ would be exactly superimposed. So, if the two individuals have equal volumes, about one half of the reflections (462) are needed to prove the correctness of the structural model here proposed. Close analogies (concerning chemistry, symmetry and parameters) with two other salts (Scordari, 1980a, 1981) convinced us that in the title compound there were $\left[\mathrm{Na}_{2} \mathrm{~K}_{2} \mathrm{Fe}_{6}^{3+}\right.$ $\mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{16-}$ sandwich sheets (simplified formula). This assumption and the sequences put forward by Scordari (1980b) were taken into account when the Patterson map was analysed.

The atomic parameters used to calculate $F_{c}$ are those of salt $X$ (Scordari, 1980a) and of its topotactic product (Scordari, 1981) duly adapted to the $c$ length. The first were employed for the atoms belonging to the sandwich sheets, the latter to characterize the intersandwich-sheet atomic content. So the structure factors for the twin $\left|\left|F_{c, T(h k l)}\right|\right\rfloor$ could be calculated according to $\left|F_{c, T(h k l)}^{c,(h)}\right|=\left[Y\left|F_{c(h k l)}\right|^{2}+(1-Y)\left|F_{c(k h i)}\right|^{2}\right]^{1 / 2}$ where $Y$ is the volume fraction of one individual and $1-Y$ is that of the other. $R=\langle |\left|F_{o, T(n k)}\right|-\left|F_{c, T(k k))}\right| \mid$ © 1983 International Union of Crystallography

$$
\left(\mathrm{Na}_{0 \cdot 12}, \mathrm{H}_{3} \mathrm{O}^{+}{ }_{0 \cdot 38}, \mathrm{H}_{2} \mathrm{O}_{0 \cdot 50}\right)_{6}\left(\mathrm{Na}_{0 \cdot 12}, \mathrm{H}_{3} \mathrm{O}^{+}{ }_{0 \cdot 88}\right)\left[\mathrm{K}_{2}\left(\mathrm{~K}_{0 \cdot 333}, \mathrm{H}_{2} \mathrm{O}_{0 \cdot 667}\right)_{6} \mathrm{Na}_{2} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12} \cdot 6 \mathrm{H}_{2} \mathrm{O}\right]
$$

$\sum\left|F_{o, T(h k l)}\right|$ for 462 reflections has a best value of 0.12 for $Y=0.48$.*

Discussion. Non-refined atomic coordinates are shown in Table 1. In Table 2 only $Q-\mathrm{O}$ and $M-\mathrm{O}$ distances are given, those missing being given in the paper on salt $X$.

The crystal structure is made up of sandwich sheets with composition $\left[\mathrm{Na}_{2} \mathrm{~K}_{2} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{6-}$ enclosing some disordered atoms labelled $P\left(\mathrm{~K}, \mathrm{H}_{2} \mathrm{O}\right)$. For the description of these sheets the reader is referred to Scordari (1980a). Here we deal essentially with three sites affected by disorder and indicated in Fig. 1, such as $M\left(\mathrm{Na}, \mathrm{H}_{3} \mathrm{O}^{+}\right), P\left(\mathrm{~K}, \mathrm{H}_{2} \mathrm{O}\right)$ and $Q\left(\mathrm{Na}, \mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{H}_{2} \mathrm{O}\right)$. According to Scordari (1977) the $\mathrm{Na}-\mathrm{K}$ replacement, concerning the atoms between $\left[\mathrm{KFe}^{3+} \mathrm{O}\left(\mathrm{SO}_{4}\right)_{6}{ }^{-}\right.$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}\right]^{4+}$ sheets, has a quite linear effect on the $c$ parameter of the title compound. Owing to the similar atomic radius with K , this result can also be extended to $\mathrm{H}_{3} \mathrm{O}^{+}$cations. So, the ratio $\mathrm{Na} /\left(\mathrm{K}+\mathrm{H}_{3} \mathrm{O}^{+}\right)=0.163$ has been inferred for $c=35.971 \AA$. Since the $\mathrm{Na} \rightarrow\left(\mathrm{K}, \mathrm{H}_{3} \mathrm{O}^{+}\right)$replacement does not affect constants $a$ and $b$, we can assume that the Na and K atoms, belonging to the $\left[\mathrm{Na}_{2} \mathrm{~K}_{2} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{6-}$ sandwich sheet, are never replaced. If so, according to the quoted ratio and in order to make $\mathrm{Na}+\mathrm{K}+$ $\mathrm{H}_{3} \mathrm{O}^{+}=10$, the lacking positive charges must be distributed as follows: $\mathrm{Na}=0.84$ and $\mathrm{K}+\mathrm{H}_{3} \mathrm{O}^{+}$ $=5 \cdot 16$. Previous structural analyses and Fourier syntheses suggested that we could assign K to $P$ and both Na and $\mathrm{H}_{3} \mathrm{O}^{+}$to $M$ and $Q$ sites.

The crystal-chemical formula which ensues is $Q_{6}$ $M\left[\mathrm{~K}_{2} P_{6} \mathrm{Na}_{2} \mathrm{Fe}_{6}^{3+} \mathrm{O}_{2}\left(\mathrm{SO}_{4}\right)_{12} .6 \mathrm{H}_{2} \mathrm{O}\right]$, where $Q$ is $\left(\mathrm{Na}_{0.12}, \mathrm{H}_{3} \mathrm{O}^{+}{ }_{0.38}, \mathrm{H}_{2} \mathrm{O}_{0.50}\right), M$ is $\left(\mathrm{Na}_{0.12}, \mathrm{H}_{3} \mathrm{O}^{+}{ }_{0.88}\right), P$ is $\left(\mathrm{K}_{0.333}, \mathrm{H}_{2} \mathrm{O}_{0.667}\right)$. In square brackets is given the chemical composition of the sandwich sheet, while the part labelled $Q$ and $M$ is an intersandwich layer of atoms.

The quoted formula can be usefully compared with a similar formula given for another compound by Scordari (1981), in which $Q$ is $\left(\mathrm{Na}_{0.38}, \mathrm{H}_{3} \mathrm{O}_{0.12}^{+}\right.$, $\left.\mathrm{H}_{2} \mathrm{O}_{0.50}\right)_{6}, M$ is K , and $P$ as above. The differences concern the $M$ site, filled by Na and $\mathrm{H}_{3} \mathrm{O}^{+}$in the title compound and by K in the other, and the $Q$ sites having reversed $\mathrm{Na} / \mathrm{H}_{3} \mathrm{O}^{+}$ratios.

This last difference seems to be responsible for the lengthening of parameter $c: \frac{1}{2} c=17.99 \AA$ (this compound) $<\frac{1}{3} c_{h}=17.32 \AA$ (salt quoted in Scordari, 1981).

The structural results confirm that the last sequence depicted by Scordari (1980b) is correct. Though, from an energy viewpoint, this sequence seemed less

[^0]favoured, we wish to point out that the distance between two opposite $\mathrm{Fe}^{3+}$ clusters belonging to two neighbouring sandwich sheets is greater here than in other compounds: 9.7 against about $9 \AA$ in another salt (Scordari, 1981) and $9.5 \AA$ in $\alpha$-Maus's salt (Giacovazzo et al., 1975).

Table 1. Positional parameters and isotropic temperature factors obtained from salt $X$ (Scordari, 1980a) and its topotactic product (Scordari, 1981), and suitably fitted for the present structure

|  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: |
|  | $x$ | $y$ | $z$ | $B\left(\AA^{2}\right)$ |
| Fe | 0.4464 | 0.1657 | 0.8842 | 0.87 |
| $\mathrm{~S}(1)$ | 0.5950 | 0.5880 | 0.6714 | 1.69 |
| $\mathrm{~S}(2)$ | 0.5960 | 0.5676 | 0.5560 | 1.37 |
| K | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.6127 | 2.79 |
| Na | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.5082 | 2.00 |
| $\mathrm{O}(1)$ | $\frac{2}{3}$ | $\frac{1}{3}$ | 0.6157 | 1.37 |
| $\mathrm{O}(2)$ | 0.7541 | 0.6047 | 0.6626 | 2.11 |
| $\mathrm{O}(3)$ | 0.7207 | 0.6385 | 0.5863 | 1.67 |
| $\mathrm{O}(4)$ | 0.4699 | 0.4063 | 0.5694 | 2.36 |
| $\mathrm{O}(5)$ | 0.4725 | 0.4623 | 0.6463 | 2.37 |
| $\mathrm{O} w(6)$ | 0.2007 | 0.2191 | 0.6159 | 2.61 |
| $\mathrm{O}(7)$ | 0.5271 | 0.6708 | 0.5518 | 1.99 |
| $\mathrm{O}(8)$ | 0.6676 | 0.5224 | 0.5226 | 2.50 |
| $\mathrm{O}(9)$ | 0.5965 | 0.7365 | 0.6629 | 3.06 |
| $\mathrm{O}(10)$ | 0.5559 | 0.5433 | 0.7108 | 3.79 |
| $P$ | 0.1854 | 0.1682 | 0.0343 | 2.68 |
| $Q$ | 0.0 | 0.22 | 0.27 | 2.68 |
| $M$ | $\frac{1}{3}$ | $\frac{2}{3}$ | 0.25 | 3.70 |

Table 2. Distances ( $\AA$ ) concerning $Q-\mathrm{O}$ and $M-\mathrm{O}$ polyhedra

For distances not given here see Scordari (1980a).

| $Q-\mathrm{O}(2,3)$ | 3.21 | $M-\mathrm{O}(10,5) \times 3$ | 3.06 |
| :--- | :--- | :--- | :--- |
| $Q-Q(12) \times 2$ | 2.56 | $M-\mathrm{O}(10,8) \times 3$ | 3.06 |
| $Q-\mathrm{O}(10,8)$ | 3.07 |  |  |
| $Q-\mathrm{O}(10,5)$ | 3.25 |  |  |



Fig. 1. The structure includes disordered atoms which are labelled $P, Q$ and $M$. According to the results inferred by crystallochemical considerations $P$ is filled by K and $\mathrm{H}_{2} \mathrm{O}, Q$ by Na , $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{H}_{2} \mathrm{O}$, and $M$ by Na and $\mathrm{H}_{3} \mathrm{O}^{+}$. Fractional heights on the $z$ axis $\left(\times 10^{2}\right)$ are also given.

As far as the sandwich-sheet relationships between the title compound and salt $X$ are concerned, we notice that two $\mathrm{Fe}^{3+}$ clusters belonging to two adjacent sandwich sheets are differently related. In fact, in our compound they are opposite and rotated with respect to each other by about $30^{\circ}$; in salt $X$ the same clusters are shifted with respect to each other by $\pm\left(\frac{1}{3} \mathbf{a}-\frac{1}{3} \mathbf{b}\right)$ and are rotated by about $60^{\circ}$.

The last question concerns the decrease of stability with the lowering of the $\mathrm{Na} / \mathrm{K}$ ratio. Briefly, this effect is connected with the shortening of the distance between opposite $\mathrm{Fe}^{3+}$ clusters caused by the replacement
$\mathrm{Na} \rightarrow\left(\mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{K}\right)$, which in turn causes an increase in the potential energy.

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# Diphosphure de Trirhodium, $\mathbf{R h}_{3} \mathbf{P}_{\mathbf{2}}$ : Premier Exemple d'une Structure Lacunaire Ordonnée de Type anti- PbFCl 

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Abstract. $M_{r}=370 \cdot 7$, tetragonal, $P \overline{4} m 2, a=3.327$ (1), $c=6.151(3) \AA, \quad V=68.1(1) \AA^{3}, \quad Z=1, \quad D_{x}=$ $9.04 \mathrm{Mg} \mathrm{m}^{-3}, \lambda(\mathrm{Mo} K \alpha)=0.71069 \AA, \mu=18.6 \mathrm{~mm}^{-1}$, $F(000)=165, T=291 \mathrm{~K}, R=0.044$ for 181 reflections. The structure shows for the first time ordered vacancies in an anti-PbFCl-type structure; indeed, $\mathrm{Rh}(1)$ atoms occupy all the square-pyramidal phosphorus sites and $\mathrm{Rh}(2)$ atoms only half of the regular tetrahedral phosphorus sites. The structural relationship with $\mathrm{Cr}_{2} \mathrm{As}$ (anti- PbFCl type) is also discussed.

Introduction. Nos travaux sur les phosphures ternaires de rhodium et d'éléments de transition $3 d$ nous ont conduits, en étude prèliminaire, à reprendre le système binaire rhodium-phosphore dans lequel seuls trois composés ont fait antérieurement l'objet d'études structurales satisfaisantes: $\mathrm{Rh}_{2} \mathrm{P}$ (Zumbusch, 1940), $\mathrm{Rh}_{4} \mathrm{P}_{3}$ (Rundqvist \& Hede, 1960), $\mathrm{RhP}_{3}$ (Rundqvist \& Ersson, 1968).

Nous avons pour notre part redéterminé sur monocristal la structure du binaire $\mathrm{RhP}_{2}$ qui n'avait été qu'amorcée précédemment (Kjekshus, 1971) et isolé deux nouveaux phosphures, l'un RhP de structure type MnP (El Ghadraoui, 1982), l'autre $\mathrm{Rh}_{3} \mathrm{P}_{2}$ dont la structure fait l'objet du présent travail.

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Partie expérimentale. Monocristaux de $\mathrm{Rh}_{3} \mathrm{P}_{2}$ obtenus par technique de flux à l'étain dans un rapport atomique $\mathrm{Rh}: \mathrm{P}: \mathrm{Sn}$ de 3:2:20. Ampoule de silice scellée sous vide, portée à 1423 K une semaine et refroidie lentement ( $5 \mathrm{~K} \mathrm{~h}^{-1}$ ) jusqu'à l'ambiante. Excès d'étain dissous dans HCl dilué qui n'affecte pas les monocristaux formés. Forme parallélépipédique, monocristal étudié: $0.05 \times$ $0.03 \times 0.01 \mathrm{~mm}$, paramètres cristallins affinés sur Nonius CAD-4 à l'aide de 25 réflexions indépendantes, monochromateur de graphite; réflexions de référence: 003 et $111 ; 248$ réflexions avec $\theta<40^{\circ}, 0 \leq h \leq 5$. $0 \leq k \leq 5, \quad 0 \leq l \leq 11,181$ réflexions indépendantes avec $I>3 \sigma(I)$, correction de Lp, absorption ignorée, méthode de Patterson pour $R h(1)$ et $P$, synthèsedifférence pour $\mathrm{Rh}(2)$, affinement base sur $F$, facteurs de température anisotropes, extinction secondaire $\left(2 \times 10^{-6}\right), R: 0 \cdot 044, R_{n}: 0 \cdot 046, w=1 / \sigma^{2}(F)$. Les facteurs de diffusion sont ceux de International Tables for X-ray Crystallography (1974). Les programmes $S D P$ (Frenz, 1978)* ont été utilisés.

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[^0]:    * Lists of structure factors for $Y=0.48$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38728 ( 9 pp .). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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