

The Structure of Pentarubidium Triaqua- μ_3 -oxo-hexa- μ -sulfato-triferrate(III) Dihydrate

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(Received 29 November 1979; accepted 21 January 1980)

Abstract

The crystal structure of $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ has been determined as part of studies on alkali iron(III) sulfate hydrates. The title compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 14.361$ (3), $b = 16.033$ (3), $c = 12.651$ (3) Å, $\beta = 92.04$ (1)°, $Z = 4$. The structure was refined to $R = 0.056$ for 2296 observed reflections. It consists of discrete trinuclear $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ units in which three FeO_6 octahedra share one common corner *via* an oxo O atom and are further linked by three pairs of bridging bidentate SO_4 groups. These units are connected by Rb^+ ions to form layers parallel to the cleavage plane (101). The layers are connected by the remaining two Rb^+ ions and two water molecules. The general structure type resembles that of $\beta\text{-K}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$ [Mereiter & Völlenklee (1978). *Acta Cryst.* B34, 378–384]. Average bond lengths are $\text{S}-\text{O} = 1.468$ and $\text{Fe}-\text{O} = 2.006$ Å for all types of O and 1.929 Å for the oxo O atom coordinated by three Fe. The structure of $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ exhibits a pseudosymmetry which leads to a subcell with $(a + c)/2 = 9.40$, $b = 16.03$, $(c - a)/2 = 9.74$ Å, $\beta = 97.3^\circ$ and pseudo space group $P2_1/m$. Several salts which are isomorphous and essentially isostructural with $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$, but contain Cs with K, NH_4 or Rb instead of five Rb, are disordered and adopt this subcell as the unit cell. Selected data on these salts are given.

Introduction

This work is part of a study on salts in the system $A_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-H}_2\text{O}$, where $A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$ or Tl , or combinations thereof. A bewildering number of salts with different chemical compositions and different crystallographic properties are obtained on evaporation of aqueous solutions of alkali sulfates with $\text{Fe}_2(\text{SO}_4)_3$ at temperatures below 373 K. Very few are presently well known in the literature (*Gmelins Handbuch der Anorganischen Chemie*, 1932). Among these salts is a group having the general composition

$A_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot n\text{H}_2\text{O}$, with $n = 5\text{--}10$. One of them, Maus's salt, $\alpha\text{-K}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$ (Giacovazzo, Scordari & Menchetti, 1975), and the closely related mineral metavoltine, $\text{K}_2\text{Na}_6\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_2\text{-}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$ (Giacovazzo, Scordari, Todisco & Menchetti, 1976), have been shown to contain the trinuclear units $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$. In our last paper we presented the crystal structure of $\beta\text{-K}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$, a monoclinic, stable polymorph of Maus's salt (Mereiter & Völlenklee, 1978). Here we present the structure of $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ and data on some isomorphous salts.

Experimental

Solutions of 3 g Rb_2SO_4 and 4 g $\text{Fe}_2(\text{SO}_4)_3$ in 30 ml H_2O yield at room temperature pale-pink crystals of the alum $\text{RbFe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. If these solutions are evaporated at 368 K, however, yellowish-brown crystals of the title compound are obtained. After the crystals have been removed from the solution and dried between pieces of filter paper they are stable in air. The chemical formula $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ was established by standard analytical techniques and later confirmed by the structure determination. Crystal data are compiled in Table 1. The crystals are platy rhombi elongated parallel to **b** and terminated by the {101} and {111} faces, sometimes also by small {010} faces, with good cleavage on (101). Optical data: biaxial negative, birefringence weak, $n_x = 1.575$, $n_y = 1.578$, $n_z = 1.580$, $2V_x = 33^\circ$, X approximately normal to (101), Z parallel to **b**, $r \ll v$ [$2V_x$ for red light almost 0° , for green light ($\lambda = 520$ nm) $\sim 60^\circ$], pronounced pleochroism with Y pale yellow, X and Z golden yellow.

Table 1. Crystal data

$\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$	
Monoclinic, space group $P2_1/n$	
$a = 14.361$ (3) Å	$M_r = 1277.3$
$b = 16.033$ (3)	$Z = 4$
$c = 12.651$ (3)	$D_x = 2.91$ Mg m $^{-3}$
$\beta = 92.04$ (1)°	$\mu(\text{Mo K}\alpha) = 10.1$ mm $^{-1}$
$V = 2911.0$ Å 3	

Weissenberg photographs showed the crystals to be monoclinic with space group $P2_1/n$. All reflections with $h + l = 2n + 1$ were systematically weak which indicated an almost B -centered structure, with the pseudo space group $B2_1/m$. This can also be described as a monoclinic subcell defined by $(\mathbf{a} + \mathbf{c})/2 = 9.40$, $\mathbf{b} = 16.03$, $(\mathbf{c} - \mathbf{a})/2 = 9.74 \text{ \AA}$, $\beta = 97.3^\circ$ with pseudo space group $P2_1/m$. Exactly this kind of unit cell was found for three salts prepared under similar conditions to $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$, but with Cs and K, NH_4 or Rb instead of five Rb. These salts will be treated in more detail at the end of this paper.

A crystal of $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ with maximum dimensions $0.28 \times 0.18 \times 0.10 \text{ mm}$ was selected for X-ray data collection. Determination of accurate lattice constants and intensity measurements were made on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation (graphite monochromator) and the ω - 2θ scan mode with a scan width of 1° and a scan speed of 2° min^{-1} . Three periodically monitored reference reflections showed only insignificant intensity fluctuations. 6365 symmetry-independent reflections with $\theta < 27^\circ$ were measured and processed to obtain F_o 's uncorrected for absorption. Of these reflections, 1950 with $h + l = 2n$ and 346 with $h + l = 2n + 1$ had $I \geq 3\sigma(I)$.

Structure determination

The structure in its main features was solved with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) in the pseudo space group $B2_1/m$, *i.e.* using only reflections with $h + l = 2n$. After location of Rb, Fe and S atoms in an E map, the O atoms were found from a difference synthesis. The structure was then refined with anisotropic temperature factors to $R = 0.09$ (1950 $h + l = 2n$ reflections). At this stage the true space group $P2_1/n$ was adopted and reflections with $h + l = 2n + 1$ were included in the calculations. Highly anisotropic temperature factors of several atoms in the $B2_1/m$ structure model indicated which atoms deviate from the pseudo mirror plane most strongly. With this information and stereochemical considerations, a distorted model was derived and then refined with isotropic temperature factors for all atoms. After readjustment of some mispositioned atoms, the refinement converged slowly but without further problems. Anisotropic temperature factors were finally introduced for Rb, Fe and S. Trial calculations showed that pseudosymmetry problems could best be overcome by including reflections with $I < 3\sigma(I)$ in the calculation of the least-squares matrix. Weights $w = 1/[\sigma^2(F_o) + 0.0008F_o^2]$ were used. The final full-matrix refinement converged to $R = 0.056$ for the 2296 reflections with $I \geq 3\sigma(I)$, $R = 0.102$ for the 346 reflections with $h + l = 2n + 1$ and $I \geq 3\sigma(I)$, and $R =$

Table 2. Fractional coordinates ($\times 10^5$ for Rb, Fe, S; $\times 10^4$ for O) and isotropic thermal parameters (\AA^2)

Isotropic thermal parameters for Rb, Fe and S have been calculated from the anisotropic thermal parameters (Hamilton, 1959).

	x	y	z	B
Rb(1)	1689 (9)	24811 (11)	74126 (12)	3.21
Rb(2)	-19460 (12)	40422 (9)	57558 (12)	2.65
Rb(3)	-18985 (11)	10619 (9)	56305 (13)	2.86
Rb(4)	-13863 (12)	5956 (11)	15673 (15)	3.59
Rb(5)	-13895 (13)	44642 (12)	15504 (17)	4.55
Fe(1)	22548 (10)	24916 (13)	51167 (11)	0.98
Fe(2)	9757 (13)	35616 (11)	33533 (13)	1.19
Fe(3)	9251 (13)	14641 (11)	33300 (15)	1.11
S(1)	31700 (23)	39352 (21)	36662 (27)	1.39
S(2)	10780 (24)	41441 (20)	58095 (26)	1.36
S(3)	8873 (20)	25611 (24)	11708 (21)	1.63
S(4)	-8647 (17)	25255 (24)	38476 (20)	1.29
S(5)	30907 (24)	10479 (21)	35894 (27)	1.49
S(6)	11021 (23)	8582 (21)	57963 (25)	1.26
O(1)	3128 (6)	3357 (6)	4566 (7)	1.80
O(2)	2190 (6)	4157 (6)	3364 (7)	2.30
O(3)	3617 (7)	4705 (6)	4055 (7)	2.43
O(4)	3638 (7)	3576 (6)	2778 (8)	3.07
O(5)	1641 (6)	3366 (6)	5987 (7)	1.75
O(6)	764 (7)	4185 (6)	4686 (7)	2.25
O(7)	1677 (7)	4863 (6)	6083 (8)	2.52
O(8)	267 (7)	4111 (6)	6458 (8)	2.88
O(9)	1251 (6)	3228 (5)	1873 (7)	1.87
O(10)	672 (7)	1829 (6)	1832 (8)	2.72
O(11)	35 (8)	2845 (7)	639 (9)	3.76
O(12)	1580 (7)	2362 (6)	412 (7)	3.05
O(13)	-367 (6)	3194 (6)	3271 (7)	1.96
O(14)	-406 (6)	1714 (5)	3607 (7)	1.73
O(15)	-1825 (6)	2526 (7)	3375 (7)	2.48
O(16)	-865 (6)	2664 (6)	4953 (7)	2.54
O(17)	2208 (6)	1101 (6)	2963 (7)	1.92
O(18)	3007 (6)	1556 (6)	4550 (8)	2.43
O(19)	3278 (7)	198 (6)	3902 (7)	2.47
O(20)	3826 (7)	1376 (6)	2948 (8)	2.90
O(21)	1046 (6)	762 (5)	4633 (6)	1.45
O(22)	1570 (6)	1670 (5)	6042 (7)	1.54
O(23)	1632 (6)	172 (6)	6256 (7)	2.26
O(24)	149 (6)	905 (5)	6191 (6)	1.50
O(25)	1372 (5)	2500 (6)	3942 (6)	1.39
O(26 w)	3309 (6)	2488 (7)	6303 (6)	2.27
O(27 w)	488 (6)	4613 (5)	2564 (7)	1.53
O(28 w)	419 (6)	346 (5)	2636 (7)	1.39
O(29 w)	6660 (12)	1371 (12)	3751 (15)	9.65
O(30 w)	1577 (11)	1307 (11)	8747 (14)	8.38

0.17 ($R_w = 0.09$) for all 6365 measured reflections. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Final atomic parameters are given in Table 2, interatomic distances and angles in Table 3.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35100 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

vazzo, Scordari, Todisco & Menchetti, 1976). A view of the trinuclear unit together with its atom numbering is given in Fig. 1. One of its main features is the central oxo O(25) which connects the Fe atoms in an almost planar Fe_3O arrangement. The Fe atoms are further linked by three pairs of bridging bidentate SO_4 groups. Bonds within the $[\text{FeH}_2\text{OO}_{\text{oxo}}(\text{O}_\text{S})_4]$ octahedra can be divided into three groups: $\text{Fe}-\text{O}_{\text{oxo}} = 1.918-1.935$, $\text{Fe}-\text{O}_\text{S} = 1.987-2.038$ and $\text{Fe}-\text{OH}_2 = 2.068-2.114$ Å. The octahedra exhibit characteristic distortions, the angles $\text{O}_{\text{oxo}}-\text{Fe}-\text{O}_\text{S} = 91.7-100.0^\circ$ (average 96.3°) being considerably larger than the angles $\text{H}_2\text{O}-\text{Fe}-\text{O}_\text{S} = 78.8-86.6^\circ$ (average 83.8°). Within the SO_4 tetrahedra S—O bonds vary from 1.415 to 1.500 Å (average 1.468 Å). Sulfate O atoms which are also linked to Fe have significantly longer S—O bonds (average 1.483 Å) than the terminal sulfate O atoms (average 1.453 Å). Average bond lengths and angles within the unit agree quite well with those in $\beta\text{-K}_3\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$, although the units of both salts differ in conformation (compare Fig. 1 of this work with Fig. 1 of Mereiter & Völlenkle, 1978). Differences in conformation of $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ units are not unexpected as all polyhedral links within the units are of the corner-sharing type, rather than edge- or face-sharing. The units are therefore not rigid and can be tilted in various ways without severely distorting the FeO_6 and SO_4 polyhedral geometry. Most outstanding in this connection is the $\text{S}(4)\text{O}_4$ tetrahedron of the Rb salt which has its $\text{O}(15)-\text{O}(16)$ edge nearly parallel to the Fe_3 plane, a situation not observed to a comparable degree for any sulfate group in $\beta\text{-K}_3\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$.

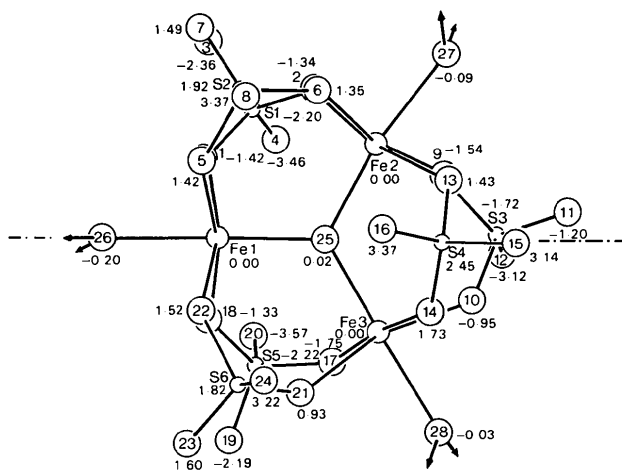


Fig. 1. Projection of an $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ unit normal to the plane defined by the three Fe atoms. The equation of the plane in terms of the unit cell is $11.218x - 0.179y - 8.245z = -1.734$. Numbers with two decimal places are heights (Å) above this plane. Standard deviations of these numbers are for Fe 0.002, for S 0.003 and for O 0.01 Å. The broken line is the n -glide plane; the arrows indicate hydrogen bonds.

The spatial arrangement of the $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ units and their connection *via* Rb^+ ions and lattice water molecules are shown in projections parallel to $[\bar{1}0\bar{1}]$ and $[10\bar{1}]$ (Figs. 2 and 3), which have been selected to show the structure most clearly. The Rb^+ ions possess irregular coordination figures and are surrounded by seven to nine O atoms at distances < 3.3 Å. The $\text{Rb}-\text{O}$ distances average 3.06 Å, which is 0.14 Å longer than the average of the $\text{K}-\text{O}$ distances in $\beta\text{-K}_3\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$. Three Rb^+ ions, $\text{Rb}(1)$ through $\text{Rb}(3)$, connect the $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ units in layers parallel to (101) , which is also the cleavage plane. The remaining two Rb^+ ions and the lattice water molecules $\text{H}_2\text{O}(29w)$ and $\text{H}_2\text{O}(30w)$

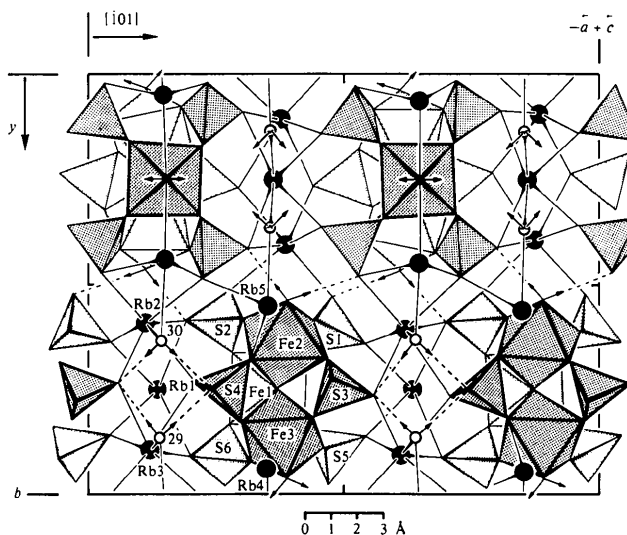


Fig. 2. $\text{Rb}_3\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$: a view of the structure parallel to $[\bar{1}0\bar{1}]$.

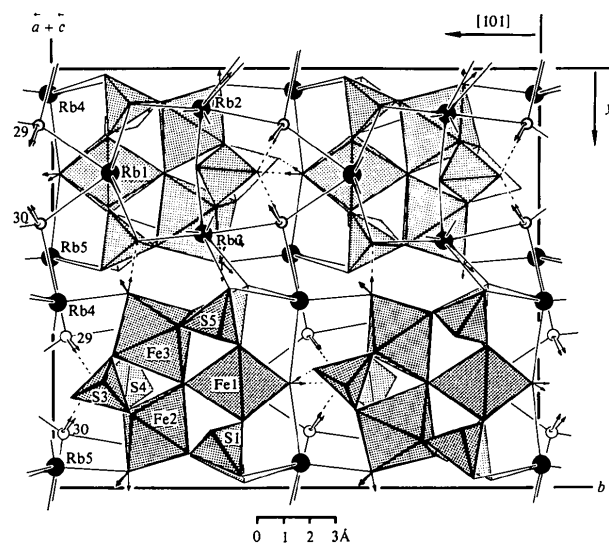


Fig. 3. $\text{Rb}_3\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$: a view of the structure parallel to $[10\bar{1}]$.

occupy channel-like spaces within the structure and establish connections normal to (101). All water molecules are involved in hydrogen bonds which could be unambiguously derived by stereochemical arguments and are listed in Table 3(e). The water molecules of the trinuclear unit form short H bonds of about 2.7 Å. Considerably longer H bonds, with average $\text{O} \cdots \text{O} = 2.9$ Å, are formed by $\text{H}_2\text{O}(29w)$ and $\text{H}_2\text{O}(30w)$, both of which also have weak interactions with three Rb.

Fig. 1 shows that the $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ unit deviates considerably from mirror symmetry. To make the n -glide plane in this figure a true mirror plane all O atoms would have to be moved by 0.01–0.55 Å (average 0.19 Å); corresponding shifts required for the Rb, Fe and S atoms are smaller, 0.01–0.12 Å. The pseudosymmetry of the structure is therefore due not so much to a pronounced pseudosymmetry within the trinuclear units, as to the special arrangement of the units with respect to the n -glide planes.

$\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ is structurally related to, but not isostructural with, $\beta\text{-K}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$. The arrangement of the $[\text{Fe}_3(\text{H}_2\text{O})_3\text{O}(\text{SO}_4)_6]^{5-}$ units is basically the same in both salts with one important difference: In the Rb salt the $\text{Fe}(1)\text{O}_6$ octahedra within one row parallel to $[\bar{1}01]$ point alternately either all up or all down (Fig. 2); in the K salt every other trinuclear unit is reversed so that the $\text{Fe}(1)\text{O}_6$ octahedra point alternately up or down within the corresponding row, here parallel to $[010]$. This can be visualized by exchanging the upper left trinuclear unit in Fig. 2 with the lower right. $\beta\text{-K}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$ also differs from the Rb salt in the arrangement of the alkali ions and lattice water molecules. The Rb^+ ions between the trinuclear units, $\text{Rb}(1)$ through $\text{Rb}(3)$, have to be replaced by five K and one H_2O . The channel-like spaces of the Rb salt are also present in the K salt, but are larger here; instead of two Rb and two H_2O they are occupied in the K salt by six H_2O in positions which would be close to the positions of the replaced atoms in the projection shown in Fig. 3. The close structural relationships are also expressed in the lattice parameters. Those of $\beta\text{-K}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 10\text{H}_2\text{O}$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.49$, $b = 18.47$, $c = 18.11$ Å, $\alpha = 90$, $\beta = 92.4$, $\gamma = 90^\circ$, $V = 3172$ Å³ are equivalent to $(a + c)/2 = 9.40$, $(c - a) = 19.74$, $b = 16.03$ Å, $[101] \wedge [010] = 90^\circ$, $[\bar{1}01] \wedge [010] = 90^\circ$, $[101] \wedge [\bar{1}01] = 97.3^\circ$, $V = 2911$ Å³ in the Rb salt.

Isomorphous salts

Three isomorphous variants of $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ could be obtained: $\text{Cs}_{5-x}\text{A}_x\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$, where $A = \text{K}$, NH_4 , or Rb and $x \approx 2$. They were prepared by evaporation at 363 K of solutions containing 3 g

$\text{Fe}_2(\text{SO}_4)_3$ and 1.8 g Cs_2SO_4 with either 1.3 g K_2SO_4 , 1 g $(\text{NH}_4)_2\text{SO}_4$ or 2 g Rb_2SO_4 in 30 ml H_2O . Platy rhombi similar in appearance to the crystals of the title compound were obtained; with the Cs–K and Cs– NH_4 salts the formation of minor amounts of small crystals with similar chemical composition but different crystallographic properties was noted several times. Attempts to replace the Rb of the title compound by only one other kind of alkali ion, Li, Na, K, NH_4 , Cs or Tl, led to different types of salts, as did attempts with combinations of two alkali ions other than those given above.

X-ray examination by Weissenberg photographs and with the four-circle diffractometer showed the three mixed salts to be monoclinic, space group $P2_1/m$ or $P2_1$, $Z = 2$, with $a \approx 9.6$, $b \approx 16.2$, $c \approx 9.8$ Å, $\beta \approx 97^\circ$, equivalent to the subcell of $\text{Rb}_5\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ ($a = 9.40$, $b = 16.03$, $c = 9.74$ Å, $\beta = 97.3^\circ$). A careful search for superstructure reflections was made but none could be detected. Optical examinations of larger crystals showed undulous extinction and sector zoning, indicating disorder phenomena. Sometimes features resembling polysynthetic twinning parallel to (010) were also observed.

A small optically homogeneous crystal of the Cs–K salt was used for collecting X-ray data under conditions similar to those for the title compound. Statistical tests indicated centrosymmetry and hence space group $P2_1/m$. The structure determination carried out in this space group ($R = 0.081$ for 1990 reflections, anisotropic temperature factors) yielded the following results: $\text{Cs}_{5-x}\text{K}_x\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$ is essentially isostructural with the title compound but with mirror planes instead of the pseudo mirror n -glide planes; the structure is disordered, as indicated by high anisotropic temperature factors (U_{22} up to 0.32 Å²) for those atoms which most violate the mirror symmetry in the title compound, particularly the $\text{S}(3)\text{O}_4$ group (Fig. 1). Owing to disorder, unusually short S–O bonds of 1.36–1.48 Å (average 1.445 Å) were encountered. Most interesting was the result that the Cs^+ and K^+ ions are preferentially distributed: At least 90% of the Cs^+ ions occupy the $\text{Rb}(2)$ and $\text{Rb}(3)$ positions with K^+ predominating in the $\text{Rb}(1)$, $\text{Rb}(4)$ and $\text{Rb}(5)$ positions.

One reason for the observed disorder of these mixed salts might be that they, as well as the title compound, are very loosely packed: The volume per formula unit in this series of salts is 728–750 Å³ and thus more than 40 Å³ larger than in another structurally different series with the composition $\text{K}_{5-x}\text{A}_x\text{Fe}_3\text{O}(\text{SO}_4)_6 \cdot 5\text{H}_2\text{O}$, where $A = \text{NH}_4$, Rb , Cs or Tl and $x \approx 2-3$ (Mereiter, 1980).

We thank Professor Dr A. Preisinger for support and discussions and Mrs C. L. K. Jelinek for technical assistance. The work was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (project

2178). Calculations were performed at the Inter-universitäres Rechenzentrum Wien with the program systems *MULTAN* 74 and *XRAY* 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

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The Structure of Potassium Thallium Triaqua- μ_3 -oxo-hexa- μ -sulfato-triferrate(III) Dihydrate, $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$

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(Received 29 November 1979; accepted 21 January 1980)

Abstract

$K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$ belongs to a new series of isomorphic salts $K_{5-x}A_xFe_3O(SO_4)_6 \cdot 5H_2O$, where $A = NH_4, Rb, Cs$ or Tl and $x \approx 2-3$. The crystal structure has been refined to $R = 0.051$ for 2900 reflections. The crystals are monoclinic, space group $P2_1/n$, $a = 16.272$ (8), $b = 10.603$ (4), $c = 17.234$ (8) Å, $\beta = 113.35$ (3)°, $Z = 4$. The structure contains discrete $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units in which three FeO_6 octahedra share common corners *via* an oxo O atom and are further linked by three pairs of bridging bidentate SO_4 groups. The units are more distorted than in all previously known examples. Alkali ions with irregular coordination figures and two lattice water molecules connect the units in a framework. The five different alkali-ion sites are statistically occupied by K and Tl. One is almost exclusively occupied by K, another by Tl and the remaining three sites by K and Tl in roughly equal amounts. The structure is the first known example where $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units, with respect to the planes through their three Fe atoms, are neither exactly nor nearly parallel throughout the structure, but occur in two inclined symmetry-related orientations.

0567-7408/80/061283-06\$01.00

Introduction

In the course of continuing studies on salts in the system $A_2SO_4-Fe_2(SO_4)_3-H_2O$, where $A = Li, Na, K, Rb, Cs, NH_4$ or Tl or combinations thereof, the structures of $\beta-K_5Fe_3O(SO_4)_6 \cdot 10H_2O$ and $Rb_3Fe_3O(SO_4)_6 \cdot 5H_2O$ have been investigated (Mereiter & Völlenklee, 1978, 1980). The present paper deals with $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$, a member of a novel series of isomorphic salts $K_{5-x}A_xFe_3O(SO_4)_6 \cdot 5H_2O$, where $A = NH_4, Rb, Cs$ or Tl and $x \approx 2-3$. These salts are structurally different from previously known related salts.

Experimental

Crystals of the title compound were grown by slow evaporation at 353 K of solutions containing 2.5 g Tl_2SO_4 , 1.3 g K_2SO_4 and 3 g $Fe_2(SO_4)_3$ in 30 ml of water. Crystallization usually starts with the formation of brown hexagonal prisms of Tl-containing Maus's salt, $\alpha-K_5Fe_3O(SO_4)_6 \cdot 10H_2O$, and continues with the formation of the title compound. After both salts have been removed from the solutions and dried between

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