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

BY KURT MEREITER

Institut für Mineralogie, Kristallographie und Strukturchemie, Technische Universität Wien, Getreidemarkt 9, A-1060 Wien, Austria

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Abstract

$K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6.5H_2O$ belongs to a new series of isomorphic salts $K_{5-x}A_xFe_3O(SO_4)_6.5H_2O$, where A = NH_4, Rb, Cs or Tl and $x \simeq 2$–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, β = 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.

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 β-$K_5Fe_3O(SO_4)_6.10H_2O$ and $Rb_5Fe_3O(SO_4)_6.5H_2O$ have been investigated (Mereiter & Völlenkle, 1978, 1980). The present paper deals with $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6.5H_2O$, a member of a novel series of isomorphic salts $K_{5-x}A_xFe_3O(SO_4)_6.5H_2O$, where A = NH_4, Rb, Cs or Tl and $x \simeq 2$–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, α-$K_5Fe_3O(SO_4)_6.10H_2O$, 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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Table 1. *Crystal data*

$K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6.5H_2O$
Monoclinic, space group $P2_1/n$

a = 16·272 (8) Å	M_r = 1435·5
b = 10·603 (4)	Z = 4
c = 17·234 (8)	D_x = 3·49 Mg m^{-3}
β = 113·35 (3)°	μ(Mo $K\alpha$) = 16·5 mm^{-1}
V = 2729·9 Å^3	

pieces of filter paper, the hexagonal crystals cloud quickly and decompose by dehydration to a yellow powder, while the crystals of the title compound are stable in air and can be separated by hand. Isomorphous salts with NH_4, Rb or Cs instead of Tl were obtained under similar conditions; for the K–Cs salt a second polymorph with the $Rb_5Fe_3O(SO_4)_6.5H_2O$-type structure (Mereiter & Völlenkle, 1980) was also observed. The chemical composition of the title compound was established by standard analytical techniques and later confirmed by the structure determination with crystals from the same batch. Preliminary investigation by Weissenberg photographs showed the crystals to be monoclinic with space group $P2_1/n$ and lattice parameters as given in Table 1. The crystals are yellowish-brown shiny prisms elongated parallel to **b** and usually terminated by the faces $\{101\}$, $\{10\bar{1}\}$ and $\{11\bar{1}\}$. Splintery fracture and an indistinctive cleavage were observed. Optical data: biaxial negative, $n \simeq 1{\cdot}66$, birefringence low, $2V_x$ large, X approximately parallel to [101], Z parallel to **b**, in transmitted light lemon yellow with weak pleochroism.

A crystal sphere 0·22 mm in diameter was mounted on a Philips PW 1100 four-circle diffractometer equipped with Mo $K\alpha$ radiation and a graphite monochromator. Accurate lattice parameters were determined from the θ values of 20 reflections. Reflection intensities were measured in the ω-scan mode with a scan width of 1°, a scan speed of 2° min^{-1} and a counter aperture of 1 × 1°. Three periodically monitored reference reflections showed negligible intensity fluctuations. 4808 symmetry-independent reflections with $3 < \theta < 25°$ were measured and 2900 with $I > 3\sigma(I)$ used for the structure analysis. The data were corrected for absorption ($\mu R = 1{\cdot}8$).

Structure determination

The positions of the heavy atoms were determined with *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) from 300 E_{hkl} with $|E| > 1{\cdot}8$, 2000 $\sum_2$ relationships, three origin-defining phases and three multisolution phases. The E map computed with the phase set which had the highest figures of merit revealed ten not very prominent maxima, which neither looked very promising nor could be assigned unambiguously to a specific atomic species. They were assumed to be Fe atoms and used in a structure factor calculation which gave R = 0·4. The subsequent Fourier synthesis yielded 14 prominent maxima, including the ten positions which were used for phasing

Table 2. *Fractional coordinates* (×10^5 *for* A = K + Tl, Fe, S; ×10^4 *for* O) *and isotropic thermal parameters* (Å^2)

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

	x	y	z	B
A(1)	1789 (6)	23599 (9)	35780 (7)	5·67
A(2)	75858 (8)	15550 (10)	17609 (8)	3·62
A(3)	14422 (8)	5777 (11)	9150 (8)	2·50
A(4)	82972 (9)	6032 (15)	47219 (8)	3·04
A(5)	40484 (19)	18867 (25)	53881 (19)	2·47
Fe(1)	61919 (12)	26365 (18)	31357 (12)	1·23
Fe(2)	44954 (12)	6335 (18)	28948 (12)	1·14
Fe(3)	41029 (12)	35559 (18)	20762 (12)	1·21
S(1)	63583 (24)	−3623 (33)	28269 (25)	1·58
S(2)	59421 (23)	14240 (35)	47307 (22)	1·43
S(3)	36292 (24)	11219 (35)	9224 (23)	1·59
S(4)	29486 (22)	23738 (33)	30614 (22)	1·35
S(5)	57206 (24)	41932 (34)	14286 (23)	1·50
S(6)	54276 (24)	53505 (33)	34987 (23)	1·54
O(1)	6601 (6)	983 (9)	2813 (6)	1·86
O(2)	5385 (6)	−438 (9)	2653 (6)	1·96
O(3)	6877 (7)	−923 (10)	3628 (7)	2·53
O(4)	6476 (7)	−1026 (10)	2147 (7)	2·67
O(5)	6493 (6)	1965 (9)	4308 (6)	1·90
O(6)	5278 (6)	572 (9)	4138 (6)	1·84
O(7)	6508 (7)	676 (11)	5444 (7)	3·38
O(8)	5481 (8)	2427 (12)	4957 (8)	3·92
O(9)	3649 (6)	444 (9)	1702 (6)	2·15
O(10)	3518 (7)	2468 (10)	1054 (7)	2·76
O(11)	2845 (7)	668 (10)	213 (7)	2·37
O(12)	4453 (8)	904 (11)	810 (8)	3·78
O(13)	3508 (7)	1259 (10)	3216 (7)	2·43
O(14)	3091 (7)	3174 (10)	2432 (7)	2·60
O(15)	2030 (7)	1992 (10)	2737 (7)	2·44
O(16)	3170 (8)	3037 (11)	3825 (8)	3·88
O(17)	4854 (6)	4350 (9)	1528 (6)	2·03
O(18)	6257 (7)	3228 (9)	2069 (7)	2·26
O(19)	6185 (7)	5394 (10)	1623 (6)	2·42
O(20)	5557 (7)	3757 (10)	591 (7)	2·84
O(21)	4517 (6)	4850 (9)	2975 (6)	2·24
O(22)	6088 (6)	4394 (9)	3485 (6)	2·15
O(23)	5573 (7)	6512 (10)	3131 (7)	2·84
O(24)	5485 (7)	5547 (10)	4349 (7)	2·55
O(25)	4940 (5)	2260 (8)	2721 (5)	1·04
O(26w)	7588 (6)	3067 (8)	3736 (6)	1·42
O(27w)	4071 (6)	−1094 (9)	3197 (6)	1·99
O(28w)	3180 (6)	4945 (9)	1369 (6)	1·89
O(29w)	7110 (10)	2264 (14)	9770 (10)	5·89
O(30w)	5981 (12)	1067 (18)	446 (12)	8·59

Occupancy factors for the A sites (A = K + Tl)

	K	Tl
A(1)	0·092 (4)	0·908 (4)
A(2)	0·407 (3)	0·593 (3)
A(3)	0·564 (3)	0·436 (3)
A(4)	0·619 (3)	0·381 (3)
A(5)	0·960 (12)	0·040 (12)
	2·64 K	2·36 Tl

Table 3. *Interatomic distances* (Å) *and angles* (°)

(*a*) Coordination of the alkali ions. The alkali-ion sites are statistically occupied by K^+ and Tl^+. (*A*—O distances ≤ 3·3 Å are given.)

A(1) = 0·09 K + 0·91 Tl

A(1)—O(2)	3·042 (10)
—O(4)	3·012
—O(17)	3·196
—O(19)	2·964
—O(23)	2·850
—O(29*w*)	3·023
Mean value	3·015

A(2) = 0·41 K + 0·59 Tl

A(2)—O(1)	2·920 (10)
—O(3)	2·972
—O(4)	3·189
—O(18)	3·002
—O(19)	2·977
—O(22)	3·288
—O(23)	2·928
—O(29*w*)	3·291
—O(30*w*)	2·745
Mean value	3·035

A(3) = 0·56 K + 0·44 Tl

A(3)—O(8)	2·757 (10)
—O(9)	3·301
—O(11)	2·979
—O(15)	3·263
—O(16)	2·763
—O(21)	3·009
—O(24)	2·793
—O(24)	2·986
Mean value	2·981

A(4) = 0·62 K + 0·38 Tl

A(4)—O(3)	2·839 (10)
—O(5)	3·091
—O(10)	2·988
—O(17)	3·140
—O(19)	2·771
—O(20)	2·898
—O(26*w*)	3·080
—O(28*w*)	2·976
Mean value	2·973

A(5) = 0·96 K + 0·04 Tl

A(5)—O(3)	2·865 (10)
—O(6)	2·820
—O(7)	3·038
—O(8)	2·773
—O(16)	2·782
A(5)—O(23)	2·920
—O(24)	2·814
—O(27*w*)	3·179
—O(29*w*)	3·038
Mean value	2·914

(*c*) SO_4 tetrahedra

				O—S—O angle
S(1)—O(1)	1·483 (11)	O(1)—O(2)	2·415 (15)	108·5 (6)
—O(2)	1·494	—O(3)	2·400	110·9
—O(3)	1·432	—O(4)	2·390	109·5
—O(4)	1·443	O(2)—O(3)	2·398	110·1
Mean value	1·463	—O(4)	2·351	106·4
		O(3)—O(4)	2·374	111·3
S(2)—O(5)	1·477 (11)	O(5)—O(6)	2·391 (15)	108·6 (7)
—O(6)	1·468	—O(7)	2·380	109·0
—O(7)	1·446	—O(8)	2·381	109·3
—O(8)	1·442	O(6)—O(7)	2·348	107·4
Mean value	1·458	—O(8)	2·398	108·9
		O(7)—O(8)	2·415	113·5
S(3)—O(9)	1·513 (11)	O(9)—O(10)	2·390 (15)	106·6 (7)
—O(10)	1·468	—O(11)	2·368	107·0
—O(11)	1·455	—O(12)	2·430	110·4
—O(12)	1·447	O(10)—O(11)	2·384	109·3
Mean value	1·471	—O(12)	2·398	110·7
		O(11)—O(12)	2·415	112·7
S(4)—O(13)	1·451 (11)	O(13)—O(14)	2·384 (15)	109·7 (7)
—O(14)	1·466	—O(15)	2·345	108·7
—O(15)	1·432	—O(16)	2·327	109·0
—O(16)	1·407	O(14)—O(15)	2·356	108·8
Mean value	1·439	—O(16)	2·356	110·2
		O(15)—O(16)	2·330	110·3
S(5)—O(17)	1·495 (11)	O(17)—O(18)	2·410 (15)	106·9 (6)
—O(18)	1·505	—O(19)	2·379	107·8
—O(19)	1·450	—O(20)	2·403	110·1
—O(20)	1·437	O(18)—O(19)	2·410	109·3
Mean value	1·472	—O(20)	2·408	109·9
		O(19)—O(20)	2·404	112·7
S(6)—O(21)	1·494 (11)	O(21)—O(22)	2·400 (15)	107·4 (6)
—O(22)	1·485	—O(23)	2·401	109·5
—O(23)	1·447	—O(24)	2·382	108·3
—O(24)	1·445	O(22)—O(23)	2·390	109·2
Mean value	1·468	—O(24)	2·414	111·0
		O(23)—O(24)	2·390	111·4

(*b*) FeO_6 octahedra

				O—Fe—O angle
Fe(1)—O(25)	1·915 (10)	O(25)—O(1)	2·971 (15)	97·7 (4)
—O(26*w*)	2·139	—O(5)	2·913	95·8
—O(1)	2·030	—O(18)	2·970	99·2
—O(5)	2·011	—O(22)	2·898	95·9
—O(18)	1·985	O(26*w*)—O(1)	2·823	85·2
—O(22)	1·986	—O(5)	2·627	78·5
Mean value	2·011	—O(18)	2·837	86·8
		—O(22)	2·700	81·6
		O(1)—O(5)	2·847	89·6
		—O(18)	2·656	82·8
		O(22)—O(5)	2·888	92·5
		—O(18)	2·845	91·5
		O(25)—O(26*w*)		173·6
		O(1)—O(22)		165·9
		O(5)—O(18)		164·0
Fe(2)—O(25)	1·939 (10)	O(25)—O(2)	2·964 (15)	97·3 (4)
—O(27*w*)	2·095	—O(6)	2·899	94·4
—O(2)	2·009	—O(9)	2·878	94·5
—O(6)	2·013	—O(13)	2·978	97·9
—O(9)	1·980	O(27*w*)—O(2)	2·743	83·8
—O(13)	2·009	—O(6)	2·661	80·7
Mean value	2·008	—O(9)	2·892	90·4
		—O(13)	2·662	80·9
		O(2)—O(6)	2·842	89·9
		—O(9)	2·804	89·3
		O(13)—O(6)	2·780	87·4
		—O(9)	2·844	91·0
		O(25)—O(27*w*)		175·0
		O(2)—O(13)		164·7
		O(6)—O(9)		171·1
Fe(3)—O(25)	1·944 (10)	O(25)—O(10)	2·896 (15)	94·4 (4)
—O(28*w*)	2·112	—O(14)	3·009	99·0
—O(10)	2·003	—O(17)	2·988	98·4
—O(14)	2·013	—O(21)	2·907	95·7
—O(17)	2·003	O(28*w*)—O(10)	2·780	85·0
—O(21)	1·978	—O(14)	2·668	80·6
Mean value	2·009	—O(17)	2·702	82·1
		—O(21)	2·763	85·0
		O(10)—O(14)	2·827	89·5
		—O(17)	2·824	89·6
		O(21)—O(14)	2·775	88·1
		—O(17)	2·809	89·8
		O(25)—O(28*w*)		179·2
		O(10)—O(21)		169·9
		O(14)—O(17)		162·6

(*d*) Coordination around the oxo O(25)

				Fe—O—Fe angle
O(25)—Fe(1)	1·915 (9)	Fe(1)—Fe(2)	3·376 (3)	122·3 (4)
—Fe(2)	1·939	—Fe(3)	3·305	117·8
—Fe(3)	1·944	Fe(2)—Fe(3)	3·360	119·8
Mean value	1·933	Mean value	3·347	

(*e*) Hydrogen bonds

O(26*w*)···O(4)	2·72 (2)	O(29*w*)···O(16)	2·82 (2)
···O(11)	2·76	···O(30*w*)	2·84
O(27*w*)···O(7)	2·89	O(30*w*)···O(12)	2·80
···O(15)	2·76	···O(12)	2·89
O(28*w*)···O(7)	2·64		
···O(15)	2·76		

the synthesis. The maxima could at this point be correctly assigned to the heavy atoms. The O atoms were then located by a difference synthesis. Atomic parameters were refined by least squares with a large-block diagonal matrix, anisotropic temperature factors for the heavy atoms and isotropic for the O atoms. For the alkali-ion sites, for which mixed occupation by K + Tl was encountered, individual occupancy factors were refined by varying the K/Tl proportion, but constraining the total occupancy factor to 1. The final agreement was $R = \sum (F_o - F_c)/\sum F_o = 0{\cdot}051$, $R_w = 0{\cdot}053$ and $S = [\sum w(F_o - F_c)^2/(2900 - 252)]^{1/2} = 1{\cdot}14$, where $w = 1/[\sigma(F_o) + 0{\cdot}02F_o]^2$. The final difference synthesis did not show unusual features. Complex neutral-atom scattering factors were used (*International Tables for X-ray Crystallography*, 1974). Final atomic parameters are given in Table 2, bond lengths and angles in Table 3.*

Discussion

$K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6.5H_2O$ and the isomorphous K–NH_4, K–Rb and K–Cs salts represent a new structure type in the family of alkali salts with the trinuclear unit $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$. The units, which are now known from more than five different types of structures (for references see below), consist of three FeO_6 octahedra which share a common corner *via* the oxo O(25) and are further linked in pairs by bridging bidentate SO_4 groups (Fig. 1). Bond lengths within the unit of the title compound (Table 3*b*,*c*,*d*) agree essentially with those in β-$K_5Fe_3O(SO_4)_6.10H_2O$ (Mereiter & Völlenkle, 1978) and $Rb_{2.74}(NH_4)_{2.26}Fe_3O(SO_4)_6.7H_2O$ (Mereiter, 1980), but are less precise. Some S–O bonds seem to be slightly short, probably because the mixed occupation of the alkali-ion sites by K and Tl introduces some disorder.

In the title compound the trinuclear unit assumes an unusual and comparatively irregular conformation. This can be seen from the heights of the terminal sulfate O(4*n* − 1), *n* = 1 through 6, above and below the plane of the Fe_3 triangle. These heights vary from 0·95 Å for O(3) to 3·24 Å for O(11) (Fig. 1), and thus extend over a wider range than the corresponding values for $Rb_5Fe_3O(SO_4)_6.5H_2O$ (Mereiter & Völlenkle, 1980), β-$K_5Fe_3O(SO_4)_6.10H_2O$ and $Rb_{2.74}(NH_4)_{2.26}Fe_3O(SO_4)_6.7H_2O$: 1·20–3·14, 1·40–2·81 and 1·45–2·24 Å, respectively. In Maus's salt, α-$K_5Fe_3O(SO_4)_6.10H_2O$ (Giacovazzo, Scordari & Menchetti, 1975), these O atoms are all at the same height of 1·96 Å, as required by the $\bar{6}$ symmetry of the unit. Such differences in conformation are, however, not surprising: each SO_4 group is attached to the unit by only two O atoms and may therefore have various orientations by changing only the Fe–O–S angles, but without modifying the FeO_6 and SO_4 polyhedral geometry. In this way the unit is able to adopt a conformation which is the most suitable for packing and for alkali coordination.

The alkali ions, 2·64 K and 2·36 Tl per formula unit, are statistically but not evenly distributed over the five different *A* sites. Two of the sites are almost exclusively occupied by either K or Tl and also differ the most in coordination figures: The *A*(1) site, occupied 91% by Tl, has an irregular coordination by only six O atoms with *A*–O distances of 2·85–3·20 Å (average 3·02 Å). The *A*(5) site, occupied 96% by K, is surrounded by nine O atoms at distances of 2·77–3·18 Å (average 2·91 Å). The trend in the average *A*–O distances of *A*(1) and *A*(5) is in reasonable agreement with the ionic radii of Tl (1·49 Å) and K (1·33 Å) (Ahrens, 1952). The remaining three *A* sites are less selectively occupied by ~40–60% K, the remainder being Tl; coordination numbers of eight to nine and average *A*–O distances of 2·97–3·04 Å are observed. The rather selective occupation of the *A*(1) and *A*(5) sites explains why two different alkali ions are necessary for the formation of the salt. Use of only one alkali ion in the preparation leads with K to two modifications of $K_5Fe_3O(SO_4)_6.10H_2O$, but with Tl to a salt presumably with ···Fe–OH–Fe–OH··· chains in the structure.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35101 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

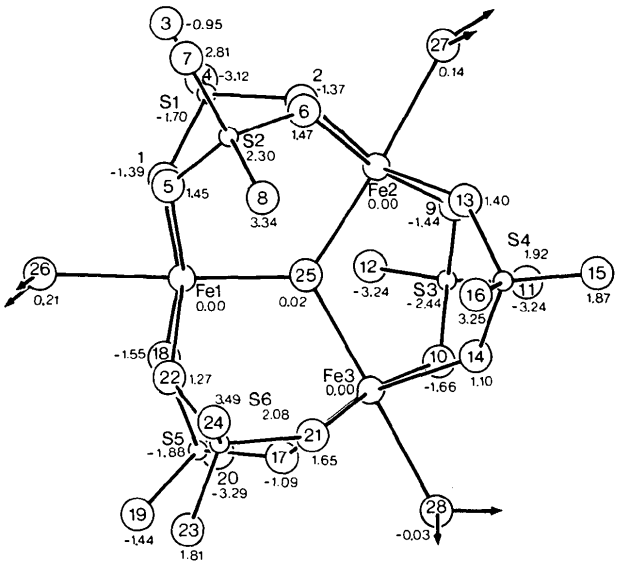

Fig. 1. Projection of an $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ unit normal to the plane defined by the three Fe atoms. The equation of the plane in terms of the unit cell is $-6{\cdot}598x + 3{\cdot}644y + 16{\cdot}172z = 1{\cdot}946$. Numbers with two decimal places are heights (Å) above this plane. Standard deviations of these numbers are for Fe 0·002, for S 0·004 and for O 0·01 Å. The arrows indicate hydrogen bonds.

For the five different water molecules of the structure hydrogen bonds could be derived by stereochemical considerations and are given in Table 3(*e*). These three molecules, which belong to the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units, have approximately tetrahedral environments, each with one Fe (Fe–O = 2·10–2·14 Å), one alkali ion (A–O = 2·98–3·18 Å) and two hydrogen-bond-accepting O atoms (O···O = 2·64–2·89 Å). Of the lattice water molecules, $H_2O(29w)$ is linked with three alkali ions (A–O = 3·02–3·29 Å), while $H_2O(30w)$ is bonded to only one alkali ion [$A(2)$–O = 2·74 Å].

The spatial arrangement of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units with respect to the alkali ions and lattice water molecules is shown in Figs. 2 and 3. In these figures the angular appearance of the units is due to their polyhedral representation. When the van der Waals radii are taken into account, the units actually approach a spherical shape. If the alkali ions and lattice water molecules are neglected, the structure can be regarded as consisting of (100) layers of hexagonal closest-packed spherical $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units (Fig. 3). Within one layer the units are oriented in such a way that the planes through their Fe_3 triangles are themselves parallel and also approximately normal to the layer plane; the orientation of a unit is further defined by an FeO_6 octahedron, in this case $Fe(1)O_6$, which points almost vertically out of the layer either up or down. Layers of basically the same type have also been observed in β-$K_5Fe_3O(SO_4)_6 \cdot 10H_2O$ and $Rb_5Fe_3O(SO_4)_6 \cdot 5H_2O$ with differences in the pattern in which the octahedra corresponding to $Fe(1)O_6$ point up or down from the layer. For a schematic comparison of the layers see Fig. 4.

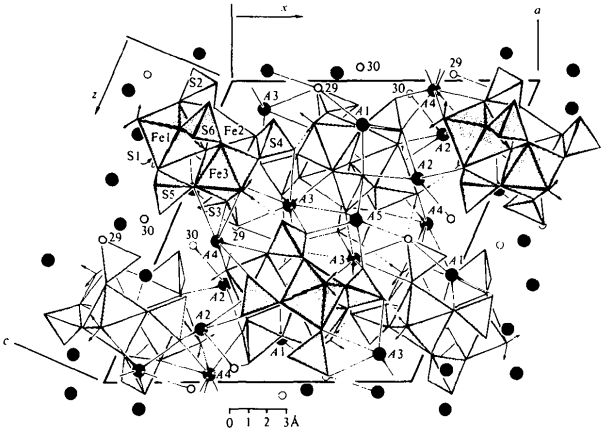

Fig. 2. The structure of $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$ viewed down **b**. The open circles are water molecules.

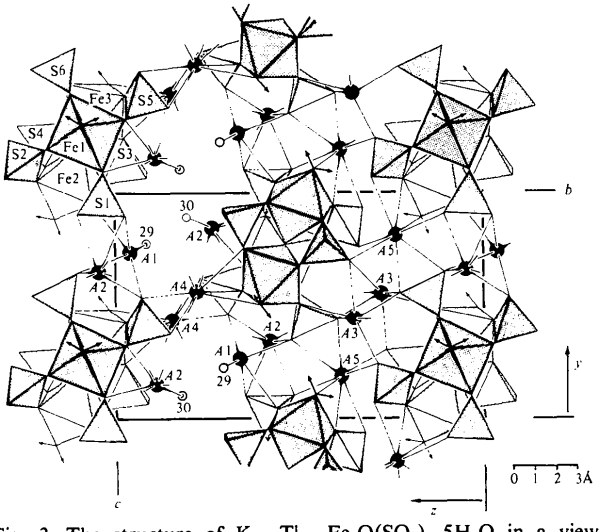

Fig. 3. The structure of $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$ in a view normal to (100). The projection is restricted to atoms within $x \sim \frac{1}{4} - \frac{3}{4}$.

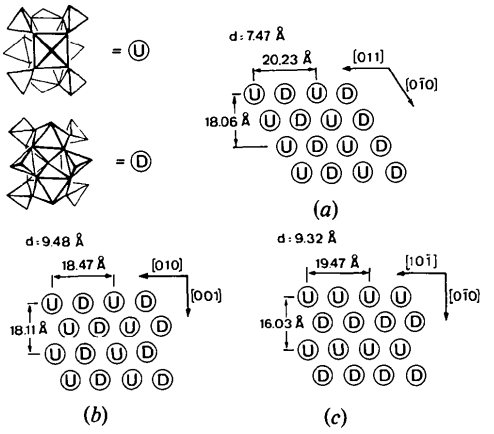

Fig. 4. Comparison of the layer-like arrangements of the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units in (*a*) $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$, (*b*) β-$K_5Fe_3O(SO_4)_6 \cdot 10H_2O$ and (*c*) $Rb_5Fe_3O(SO_4)_6 \cdot 5H_2O$. U and D represent an $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ unit in the orientations shown on the left. *d* is the layer-to-layer separation.

In β-$K_5Fe_3O(SO_4)_6 \cdot 10H_2O$ and in $Rb_5Fe_3O(SO_4)_6 \cdot 5H_2O$ the hexagonal packing scheme is only two-dimensional: The layers are stacked with the trinuclear units of one layer almost directly over those of the next layer with layer-to-layer separations of 9·48 and 9·32 Å. The spaces between the layers are occupied by water molecules and/or alkali ions. In $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$ the layers are stacked with the trinuclear units from one layer over the spaces of the other, that is in a way similar to three-dimensional closest packing with layer-to-layer separations of 7·47 Å. The structure is therefore comparatively densely packed. The volume of one formula unit, 682 Å^3, is 46 Å^3 smaller than that of $Rb_5Fe_3O(SO_4)_6 \cdot 5H_2O$, 728 Å^3.

The structure of $K_{2.64}Tl_{2.36}Fe_3O(SO_4)_6 \cdot 5H_2O$ is the first known example where the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units occur in two different orientations, inclined by 40° with respect to the planes through their Fe_3

triangles. All previously known salts contain the $[Fe_3(H_2O)_3O(SO_4)_6]^{5-}$ units in arrangements with the Fe_3 triangles parallel or almost parallel throughout the structure. This property is responsible for the pronounced pleochroism of these salts, which strongly absorb blue-green light when the electric vector of the light vibrates parallel to all Fe_3 triangles. In the title compound the pleochroism is weaker, which indicates that the Fe_3 triangles occur in more than one orientation.

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The Structure of BaCu and SrCu

BY MARIA L. FORNASINI AND FRANCO MERLO

Istituto di Chimica Fisica, Università di Genova, Corso Europa, Palazzo delle Scienze, 16132 *Genova, Italy*

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Abstract

BaCu has hexagonal symmetry with $a = 4{\cdot}499$ (3), $c = 16{\cdot}25$ (1) Å, space group $P6_3/mmc$, $Z = 4$, $D_x = 4{\cdot}68$ Mg m^{-3}, μ(Mo $K\alpha$) = 21·5 mm^{-1}. The structure has been solved by trial methods using photographic data, and refined to an R of 0·090 for 49 observed reflexions. SrCu is isomorphous, with $a = 4{\cdot}341$ (3), $c = 15{\cdot}38$ (1) Å. The structure of BaCu is formed by a sequence along [001] of slabs of trigonal prisms of Ba centred by Cu atoms and stacked in a close-packing manner. Weak Ba–Ba bonds between adjacent slabs allow BaCu to be considered as a layer compound. A close relationship with the AlB_2 and CrB types is also pointed out.

Introduction

Amongst the nine possible equiatomic binary compounds between Ca, Sr and Ba on the one hand, and Cu, Ag and Au on the other, seven phases are known to exist in the corresponding binary systems; no information is reported in the literature about the existence of the remaining two (BaAg and BaAu). As only CaAg has until now been studied structurally (Calvert, Dunsmore, Kuhi & Tse, 1957), an investigation has been undertaken to elucidate the structure of all these intermetallic compounds. The present work reports the results obtained for the phases SrCu and BaCu, the existence of which was found by Bruzzone (1971) in the study of the respective equilibrium diagrams.

Experimental

The metals used were barium and strontium from Fluka Co. (Switzerland) of 99·5 wt% purity, and copper from Koch-Light (England) of 99·999 wt% purity. The two compounds were prepared by melting stoichiometric amounts of the component metals in sealed tantalum crucibles. The slowly cooled alloys were well crystallized, with large and very thin plate-like crystals; the

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