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Structures of Potassium Sodium Sulphate and Tripotassium Sodium Disulphate

BY K. OKADA AND J. OSSAKA

Department of Inorganic Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, *Japan*

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Abstract. $KNaSO_4$: trigonal, $P3m1$, a = 5·6066 (7), c = 7·177 (1) Å, Z = 2, D_x = 2·69 Mg m^{-3}. $K_3Na(SO_4)_2$: trigonal, $P\bar{3}m1$, a = 5·6801 (6), c = 7·309 (3) Å, Z = 1, D_x = 2·70 Mg m^{-3}. Crystals of both compounds were synthesized by heating a mixture of K_2SO_4 and Na_2SO_4 in a Pt crucible at 1273 K for 2 h. Colourless transparent prismatic crystals were obtained. Both structures are built up of SO_4 tetrahedra, $M(1)O_6$ octahedra, $M(2)O_{10}$ and $M(3)O_{12}$ polyhedra. In $KNaSO_4$, Na atoms occupy the $M(1)$ and $M(2)$ and K atoms the $M(2)$ and $M(3)$ sites. In $K_3Na(SO_4)_2$, Na atoms occupy the $M(1)$ and K atoms the $M(2)$ and $M(3)$ sites.

Introduction. From Weissenberg photographs, the crystals of $KNaSO_4$ were found to have trigonal Laue symmetry $\bar{3}m$ and those of $K_3Na(SO_4)_2$ $6/mmm$. Systematic absences were not observed for either substance. The possible space groups of $KNaSO_4$ were restricted to $P3m1$, $P321$ or $P\bar{3}m1$. The crystals of $K_3Na(SO_4)_2$ were considered to be merohedral twins formed from crystals having space groups $P3m1$, $P321$ or $P\bar{3}m1$ in two orientations related by a rotation around the c axis. $P3m1$ and $P\bar{3}m1$ gave satisfactory results for the structure refinements of $KNaSO_4$ and $K_3Na(SO_4)_2$ respectively. Intensity collections were carried out using for $KNaSO_4$ a prismatic crystal with dimensions about 0·15 × 0·05 × 0·05 mm and for $K_3Na(SO_4)_2$ a nearly cubic crystal with dimensions about 0·12 × 0·12 × 0·10 mm. The ω–2θ scan technique was used to measure intensities on a Philips PW 1100 automated four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation, up to 2θ = 75° for $KNaSO_4$ and 2θ = 70° for $K_3Na(SO_4)_2$. The scan speed was 4° min^{-1} in ω and scanning was repeated twice when the total counts were less than 3000. The scan width was determined according to $(1\cdot4 + 0\cdot2\tan\theta)°$. Intensities were corrected for Lorentz–polarization factors. No absorption corrections were made, since the μR values of both crystals were less than 0·1 [μ(Mo $K\alpha$) = 0·346 for $KNaSO_4$ and 0·392 mm^{-1} for $K_3Na(SO_4)_2$]. 373 and 317 independent reflexions with $|F| > 3\sigma(|F|)$ were obtained and used for the structure determinations of $KNaSO_4$ and $K_3Na(SO_4)_2$ respectively.

The positions of all atoms of $KNaSO_4$ were obtained from Patterson maps. The structure was refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) and anisotropic thermal parameters for all atoms. The site populations of the Na and K atoms in the K(2) and Na(2) sites were also varied, but the existence of neither the Na atom in the K(2) site nor the K atom in the Na(2) site could be detected. The final value of R was 0·046.

The crystal of $K_3Na(SO_4)_2$ used for the structure determination was assumed to be a merohedral twin formed from crystals with space group $P\bar{3}m1$ in two orientations. Thus, the structure determination was carried out by a method similar to that used for $K_2W_4O_{13}$ (Okada, Marumo & Iwai, 1978). Crystals in one orientation were related to those in the other by a rotation of 180° about the c axis. In this case, the hkl reflexions of one component crystal coincide with the khl reflexions of the other in reciprocal space. The volume ratio between the crystals in the two orientations was assumed to be 1:1 because all the specimens examined always gave diffraction patterns with hexagonal Laue symmetry $6/mmm$. The parameters were refined by the least-squares procedure, using $hk0$ and hhl data of 57 reflexions which were not

Table 1. *Final positional parameters*

	x	y	z
(*a*) $KNaSO_4$			
K(3)	0	0	0
Na(1)	0	0	0·504 (3)
Na(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·689 (2)
K(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·309 (2)
S(1)	$\frac{2}{3}$	$\frac{1}{3}$	0·234 (1)
S(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·764 (1)
O(1)	$\frac{2}{3}$	$\frac{1}{3}$	0·026 (2)
O(2)	$\frac{1}{3}$	$\frac{2}{3}$	0·955 (4)
O(3)	0·187 (1)	−0·187	0·710 (2)
O(4)	0·803 (1)	−0·803	0·314 (2)
(*b*) $K_3Na(SO_4)_2$			
K(3)	0	0	0
Na	0	0	$\frac{1}{2}$
K(2)	$\frac{2}{3}$	$\frac{1}{3}$	0·6831 (2)
S	$\frac{2}{3}$	$\frac{1}{3}$	0·2338 (2)
O(1)	$\frac{2}{3}$	$\frac{1}{3}$	0·0316 (8)
O(2)	0·8073 (3)	−0·8073	0·3018 (4)

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influenced by the twinning, and used for the calculation of the structure factors of all the observed reflexions. Each of the observed intensities was then separated into the contributions from the crystals in the respective orientations according to:

$$|F_o(hkl)|^2 = \frac{[|F_o(hkl)|^2 + |F_o(khl)|^2]|F_c(hkl)|^2}{[|F_c(hkl)|^2 + |F_c(khl)|^2]},$$

$$|F_o(khl)|^2 = [|F_o(hkl)|^2 + |F_o(khl)|^2] - |F_o(hkl)|^2.$$

The structure was then refined with all the reflexion data by means of the least-squares procedure. The final value of R became 0·042 with anisotropic thermal parameters for all atoms. The atomic scattering and dispersion factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). Final positional parameters of $KNaSO_4$ and $K_3Na(SO_4)_2$ are given in Table 1.* Interatomic distances and bond angles of $KNaSO_4$ and $K_3Na(SO_4)_2$ are given in Table 2.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

(*a*) $KNaSO_4$

Symmetry code

(0)	x,y,z	(xii)	$1+x, 1+y, z$
(i)	$x, 1+y, z$	(xiii)	$x-1, x-y-1, z$
(ii)	$x, x-y-1, z$	(xiv)	$2+y-x, 2-x, z$
(iii)	$2+y-x, 1-x, z$	(xv)	$x, 2+y, z$
(iv)	$x, x-y, z$	(xvi)	$x-1, y, z$
(v)	$1+y-x, 1-x, z$	(xvii)	$x-1, y-1, z$
(vi)	$x-1, 1+y, z$	(xviii)	$x, y, z-1$
(vii)	$y-x, -x, z$	(xix)	$x-1, y-1, z-1$
(viii)	$x-1, x-y-2, z$	(xx)	$x, y-1, z-1$
(ix)	$x, y, 1+z$	(xxi)	$x, x-y, z-1$
(x)	$1+y-x, -x, z$	(xxii)	$y-x, -x, z-1$
(xi)	$x+1, x-y, z$		

SO_4 tetrahedra			
S(1)–O(1^{0})	1·496 (20)	S(2)–O(2^{0})	1·368 (29)
S(1)–O($4^{i,ii,iii}$)	1·440 (11) ×3	S(2)–O($3^{i,iv,v}$)	1·478 (9) ×3
Mean	1·454 (13)	Mean	1·451 (14)
O(1)–S(1)–O(4)	113·5 (7)	O(2)–S(2)–O(3)	105·4 (7)
O(4)–S(1)–O(4)	105·1 (7)	O(3)–S(2)–O(3)	113·2 (5)
$M(1)O_6$ octahedron			
Na(1)–O($3^{0,iv,vii}$)	2·340 (16) ×3	Na(1)–O($4^{iii,vi,viii}$)	2·349 (15) ×3
Mean	2·345 (16)		
$M(2)O_{10}$ polyhedra			
Na(2)–O(1^{ix})	2·419 (21)	Na(2)–O($4^{i,ii,iii}$)	2·994 (19) ×3
Na(2)–O($3^{0,iv,v,x,xi,xii}$)	2·814 (7) ×6		
Mean	2·829 (12)		
K(2)–O(2^{ix})	2·537 (29)	K(2)–O($3^{i,v,vi}$)	3·213 (17) ×3
K(2)–O($4^{ii,iii,vi,xiii,xiv,xv}$)	2·819 (8) ×6		
Mean	2·909 (13)		
$M(3)O_{12}$ polyhedron			
K(3)–O($1^{0,xvi,xvii}$)	3·242 (1) ×3	K(3)–O($2^{xviii,xix,xx}$)	3·253 (3) ×3
K(3)–O($3^{xviii,xxi,xxii}$)	2·761 (12) ×3	K(3)–O($4^{iii,vi,viii}$)	2·961 (14) ×3
Mean	3·054 (8)		

(*b*) $K_3Na(SO_4)_2$

Symmetry code

(0)	x,y,z	(xi)	$x-y-1, x-1, 1-z$
(i)	$x, 1+y, z$	(xii)	$2+y, 2+y-x, 1-z$
(ii)	$-y, x-y-1, z$	(xiii)	$2-x, -y, 1-z$
(iii)	$1+y-x, 1-x, z$	(xiv)	$1-x, 1-y, -z$
(iv)	$1+y, 2+y-x, 1-z$	(xv)	$y-x, 1-x, z$
(v)	$x-1, 1+y, z$	(xvi)	$-x, -y, -z$
(vi)	$x-y-2, x-1, 1-z$	(xvii)	$y-x, -x, z$
(vii)	$-y-1, x-y-2, z$	(xviii)	$x-y-1, 1-x, -z$
(viii)	$1-x, -y-1, 1-z$	(xix)	$1+y, 2+y-x, -z$
(ix)	$x, y, 1+z$	(xx)	$x-y-2, x-1, -z$
(x)	$x-y-1, x, 1-z$	(xxi)	$1-x, -y-1, -z$

SO_4 tetrahedron			
S–O(1^{0})	1·477 (6)	O(1)–S–O(2)	109·8 (1)
S–O($2^{i,ii,iii}$)	1·470 (2) ×3	O(2)–S–O(2)	109·2 (1)
Mean	1·472 (3)		
$M(1)O_6$ octahedron			
Na–O($2^{iii,iv,v,vi,vii,viii}$)	2·386 (2) ×6		
$M(2)O_{10}$ polyhedron			
K(2)–O(1^{ix})	2·547 (6)	K(2)–O($2^{i,ii,iii}$)	3·112 (3) ×3
K(2)–O($2^{iv,viii,x,xi,xii,xiii}$)	2·854 (2) ×6		
Mean	2·901 (3)		
$M(3)O_{12}$ polyhedron			
K(3)–O($1^{0,xiv,xv,xvi,xvii,xviii}$)	3·288 (1) ×6		
K(3)–O($2^{iii,v,vii,xix,xx,xxi}$)	2·908 (2) ×6		
Mean	3·098 (2)		

Discussion. It has been reported by Eysel (1973) that 'the glaserite $[(K,Na)_2SO_4]$ structure and its deformed derivatives have been found or can be predicted for $(A,C)_2BX_4$ solid solutions'. In fact, there are many substances which are reported to be isostructural with the glaserite structure. A structure determination of this type has been reported by Okada, Ossaka & Iwai (1979) for Tl_2WO_4; however, a structural investigation of the glaserite $[(K,Na)_2SO_4]$ has not yet been made.

The structures of $KNaSO_4$ and $K_3Na(SO_4)_2$ viewed along the c and a axes are shown in Figs. 1 and 2 respectively. Both structures are built up of SO_4 tetrahedra, $M(1)O_6$ octahedra, $M(2)O_{10}$ and $M(3)O_{12}$ polyhedra. The apices of neighbouring SO_4 tetrahedra point in opposite directions along the c axis. The S(1)–O and S(2)–O distances in $KNaSO_4$ range from 1·368 (29) to 1·496 (20) Å (means 1·454 and 1·451 Å), while the S–O distances in $K_3Na(SO_4)_2$ are 1·477 (6) and 1·470 (2) Å (mean 1·472 Å). In $KNaSO_4$ the O–S(1)–O angles are 105·1 (7) and 113·5 (7)°, and the O–S(2)–O angles are 105·4 (6) and 113·2 (5)°. In $K_3Na(SO_4)_2$ the O–S–O angles are 109·2 (1) and 109·8 (1)°. The distortions of the $S(1)O_4$ and $S(2)O_4$ tetrahedra of $KNaSO_4$ are very large, whereas that of the SO_4 tetrahedron of $K_3Na(SO_4)_2$ is very small. The $M(1)$ sites of both substances are occupied by Na atoms. The Na(1)–O distances in

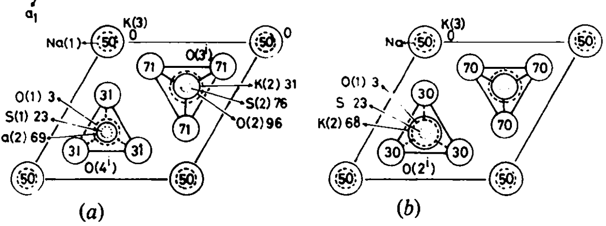

Fig. 1. The crystal structures of (*a*) $KNaSO_4$ and (*b*) $K_3Na(SO_4)_2$ viewed along the c axis. The numbers give the heights of atoms (×10^2) in decimal fractions of the c length. Large open circles denote K, medium open circles denote O and Na, and small open circles denote S atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35011 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

$KNaSO_4$ are 2·340 (16) and 2·349 (15) Å (mean 2·345 Å), and the Na—O distance in $K_3Na(SO_4)_2$ is 2·386 (2) Å. The $M(2)$ sites of $KNaSO_4$ are occupied by K and Na atoms, while those of $K_3Na(SO_4)_2$ are occupied only by K atoms. The Na(2)—O distances range from 2·419 (21) to 2·994 (19) Å (mean 2·829 Å) and the K(2)—O distances range from 2·537 (29) to 3·213 (17) Å (mean 2·909 Å) in $KNaSO_4$. The K(2)—O distances of $K_3Na(SO_4)_2$ range from 2·547 (6) to 3·112 (3) Å (mean 2·901 Å). There are fairly short Na—O and K—O distances in each $M(2)O_{10}$ polyhedron. The $M(3)$ sites of both substances are occupied by K atoms. The K(3)—O distances of $KNaSO_4$ range from 2·761 (12) to 3·253 (3) Å (mean 3·054 Å), while those of $K_3Na(SO_4)_2$ are 2·908 (2) and 3·288 (1) Å (mean 3·098 Å).

The crystal structure of glaserite has been postulated by many workers. Moore (1973) considered that the formal composition of glaserite could be written as $M(3)^{[12]}M(2)_2^{[10]}M(1)^{[6]}[T^{[4]}O_4]_2$ and that K atoms occupy the $M(2)$ sites and Na atoms the $M(1)$ and $M(3)$ sites in $KNaSO_4$. Eysel (1973), however, considered that K atoms first fill the $M(3)$ and then the $M(2)$ sites. Our structure determinations of $KNaSO_4$ and $K_3Na(SO_4)_2$ show that K atoms first fill the $M(3)$ and then go into the $M(2)$ sites while Na atoms first fill the $M(1)$ and then the $M(2)$ sites. This result is in line with the propositions of Eysel (1973) but not with those of Moore (1973). As the Na and K atoms in the $M(2)$ sites in $KNaSO_4$ are ordered, the space group of $KNaSO_4$ must be $P3m1$ and not $P\bar{3}m1$. Therefore, the formal composition of $KNaSO_4$ is written as $M(3)^{[12]}M(2)^{[10]}M(2')^{[10]}M(1)^{[6]}[T^{[4]}O_4]_2$. It can be considered that the structure of $KNaSO_4$ is an ordered derivative of glaserite and that there is a slight discontinuity between the structure of $KNaSO_4$ and that of $K_3Na(SO_4)_2$.

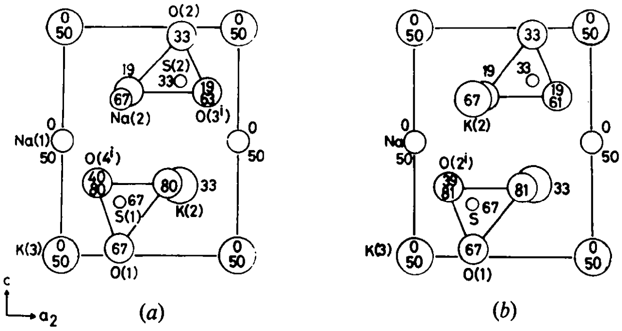

Fig. 2. The crystal structures of (*a*) $KNaSO_4$ and (*b*) $K_3Na(SO_4)_2$ viewed along the *a* axis. The numbers give the heights of atoms ($\times 10^2$) in decimal fractions of the *a* length. The atoms are depicted as in Fig. 1.

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α-Calcium Disodium Pyrophosphate Tetrahydrate

By P.-T. Cheng and K. P. H. Pritzker

Division of Pathology, Mount Sinai Hospital, Toronto, Canada M5G 1X5

and S. C. Nyburg

Lash Miller Chemical Laboratories, University of Toronto, Toronto, Canada M5S 1A1

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Abstract. α-$CaNa_2P_2O_7.4H_2O$, $M_r = 332·0$, monoclinic, Pc, $a = 5·689\ (6)$, $b = 8·586\ (8)$, $c = 10·565\ (9)$ Å, $\beta = 106·3\ (1)°$, $Z = 2$, $D_c = 2·08$ Mg m^{-3} (not measured), $\mu(Cu\ K\alpha) = 9·09$ mm^{-1}. The structure reported is one of three known polymorphs. The α and β structures contain almost identical parallel Ca^{2+}...

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