

The crystal structure determinations and refinements of $\text{K}_2\text{S}_2\text{O}_7$, KNaS_2O_7 and $\text{Na}_2\text{S}_2\text{O}_7$ from X-ray powder and single crystal diffraction data

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Abstract

The crystal structures of $\text{K}_2\text{S}_2\text{O}_7$, KNaS_2O_7 and $\text{Na}_2\text{S}_2\text{O}_7$ have been solved and/or refined from X-ray synchrotron powder diffraction data and conventional single-crystal data. $\text{K}_2\text{S}_2\text{O}_7$: From powder diffraction data, monoclinic $C2/c$, $Z = 4$, $a = 12.3653(2)$, $b = 7.3122(1)$, $c = 7.2868(1)$ Å, $\beta = 93.0792(7)^\circ$, $R_{\text{Bragg}} = 0.096$. KNaS_2O_7 : From powder diffraction data; triclinic $P\bar{1}$, $Z = 2$, $a = 5.90476(9)$, $b = 7.2008(1)$, $c = 7.4188(1)$ Å, $\alpha = 101.7074(9)$, $\beta = 90.6960(7)$, $\gamma = 94.2403(9)^\circ$, $R_{\text{Bragg}} = 0.075$. $\text{Na}_2\text{S}_2\text{O}_7$: From single-crystal data; triclinic $P\bar{1}$, $Z = 2$, $a = 6.7702(9)$, $b = 6.7975(10)$, $c = 6.7292(9)$ Å, $\alpha = 116.779(2)$, $\beta = 96.089(3)$, $\gamma = 84.000(3)^\circ$, $R_{\text{F}} = 0.033$. The disulphate anions are essentially eclipsed. All three structures can be described as dichromate-like, where the alkali cations coordinate oxygens of the isolated disulphate groups in three-dimensional networks. The K–O and Na–O coordinations were determined from electron density topology and coordination geometry. The three structures have a cation-disulphate chain in common. In $\text{K}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{S}_2\text{O}_7$ the neighbouring chains are antiparallel, while in KNaS_2O_7 the chains are parallel. The differences between the $\text{K}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{S}_2\text{O}_7$ structures, with double-, respectively single-sided chain connections and straight, respectively, corrugated structural layers can be understood in terms of the differences in size and coordinating ability of the cations.

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1. Introduction

The most widely used catalyst for SO_2 oxidation in sulphuric acid production and flue gas cleaning is under reaction conditions a molten $M_2\text{S}_2\text{O}_7$ – V_2O_5 mixture supported by a Kieselguhr carrier [1]. Classically M is a 1:3 Na:K mixture, which acts as solvent for the catalytically active vanadium complexes. Recently, the phase diagram of the $\text{Na}_2\text{S}_2\text{O}_7$ – $\text{K}_2\text{S}_2\text{O}_7$ system was constructed based on combined conductivity measure-

ments, thermal measurements and classical thermodynamic calculation [2]. To complement the constructed phase diagram, a structural investigation of the end members, $\text{Na}_2\text{S}_2\text{O}_7$ and $\text{K}_2\text{S}_2\text{O}_7$, and the tentative KNaS_2O_7 phase was performed. Only the crystal structure of $\text{K}_2\text{S}_2\text{O}_7$ was previously known [3]. A unit cell has been proposed for $\text{Na}_2\text{S}_2\text{O}_7$ [4], and the existence of an independent KNaS_2O_7 phase has been suggested [5,6]. The purpose of the present work is to present the full account of the three room-temperature crystal structures of $\text{K}_2\text{S}_2\text{O}_7$, KNaS_2O_7 and $\text{Na}_2\text{S}_2\text{O}_7$ solved and/or refined from X-ray synchrotron powder diffraction data as previously communicated [2], and

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complemented with a conventional single-crystal data collection and structure refinement of $\text{Na}_2\text{S}_2\text{O}_7$. During the course of this work it became obvious that the alkali ion coordination numbers could in general not be deduced straightforwardly from their oxygen distances only. Instead a combination of the analysis of the electron density topology, and coordination geometry arguments were used as discussed below.

2. Experimental section

Sample preparations: The end members, $\text{K}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{S}_2\text{O}_7$, were prepared by thermal decomposition of $\text{K}_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_8$ (Merck, p.a.), respectively. KNaS_2O_7 phase was prepared from a 1:1 molar $\text{Na}_2\text{S}_2\text{O}_7$ – $\text{K}_2\text{S}_2\text{O}_7$ mixture, melted and slowly cooled to room temperature. The samples for powder diffraction were ground and sealed in 0.3 mm quartz capillaries. The colourless, hygroscopic disulphate salts were handled in dry N_2 atmosphere in a glove box throughout the preparations. $\text{Na}_2\text{S}_2\text{O}_7$ single-crystals were grown from ten times zone melting in an evacuated Pyrex glass ampoule.

Powder diffraction data collection: The powder diffraction data collections were performed at beamline I711 at the MAX-II synchrotron in Lund, Sweden [7]. The diffraction patterns were recorded with a Huber G670 Guinier camera [8]. The wavelength, 1.5226(Å), was determined using a Si standard. The powdered samples were contained in 0.3 mm quartz capillaries and the data sets were accumulated for 10 min during constant sample rotation. The patterns were recorded between 10 and 100° in steps of 0.005° in 2θ . The data sets were corrected for non-linearity by a built-in calibration routine. The background from the capillary

and air scattering was subtracted from the data prior to data evaluation. The original diffraction patterns were retained and used for weighting in the Rietveld refinements.

Structure solution from powder data: The crystal structure of $\text{Na}_2\text{S}_2\text{O}_7$ was solved using EXPO [9,10] in space group $P1$. The initial Rietveld structure refinements revealed strong correlation between pairs of disulphate molecules and Na ions. A centre of symmetry could be identified and the space group settled to $P\bar{1}$. The diffraction pattern of KNaS_2O_7 was indexed as triclinic using TREOR [11]. The crystal structure could not be solved straightforwardly using EXPO. Instead, the crystal structure of $\text{K}_2\text{S}_2\text{O}_7$ was transformed into the triclinic unit cell and used for starting coordinates for the Rietveld structure refinements in space group $P\bar{1}$. The geometry of the disulphate group was heavily restrained to the idealised geometry and the refinements restricted by diagonal damping. After initial convergence the K site showed some unexpectedly short oxygen distances and one of the SO_4 groups appeared unstable. After swapping the S and K sites and locating three new O sites from a difference Fourier map, the refinements converged rapidly with expected interatomic distances.

Rietveld refinements: The Rietveld refinement program employed is a locally modified, Windows adopted version of the LHMP program [12]. The Bragg peaks were modelled with pseudo-Voigt functions with full-width at half-maximum (FWHM) described by three parameters as $(U \tan^2 \theta + V \tan^2 \theta + W)^{1/2}$, one Lorentzian contribution parameter, one asymmetry parameter and one preferred orientation parameter ($\text{K}_2\text{S}_2\text{O}_7$), and peaks limited to 18 halfwidths. The remaining background was fitted with Chebyshev polynomials, up to third order for $\text{Na}_2\text{S}_2\text{O}_7$, sixth for KNaS_2O_7 and fourth for $\text{K}_2\text{S}_2\text{O}_7$. Absorption correction for the cylindrical

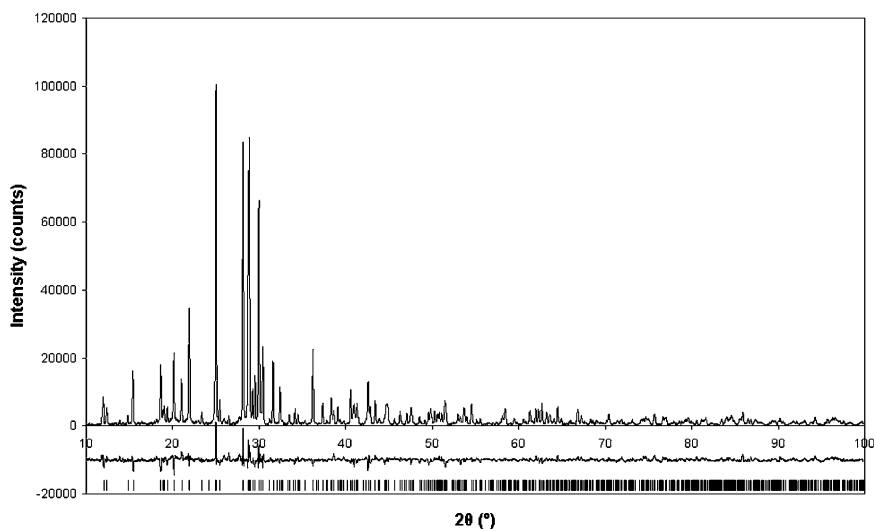


Fig. 1. Rietveld refinement plot for KNaS_2O_7 showing background subtracted raw data (top), final difference curve (middle) and Bragg peak positions (bottom).

sample was applied to the calculated Bragg intensities. All coordinates and isotropic temperature factors were individually refined except the oxygen thermal parameters in $\text{K}_2\text{S}_2\text{O}_7$ that were coupled. All Rietveld refinements were considered converged when the maximum parameter shift/e.s.d. was below 0.3. It should be noticed that due to the systematic nature of the profile fit errors, the GOF:s are relatively high for high-intensity synchrotron data. The final Rietveld fit for KNaS_2O_7 is shown in Fig. 1.

Single-crystal data collection, structure solution and refinements: A colourless crystal, $0.02 \times 0.12 \times 0.17$ mm, of $\text{Na}_2\text{S}_2\text{O}_7$ was selected for the single-crystal data collection on a Siemens/Bruker SMART 1K CCD diffractometer. The moisture-sensitive crystal was protected by a cold, 120 K, nitrogen gas stream. A total of 1962 reflections to $\theta_{\text{max}} = 29.79^\circ$ merged to 1373 unique reflections with $R_{\text{int}} = 0.0179$ after absorption correction (SADABS [13]). Data collection, integration of frame data used programs SMART and SAINT [14],

structure solution and refinement used the program SHELXTL [15]. The differences between the 293 and 120 K structures are only minor, and discussion below will be based on the 120 K structure only.

Some overall data collection and refinement parameters are given in Table 1, the final atomic parameters in Table 2, and selected interatomic distances and angles in Table 3. Further details of the crystal investigations of the new crystal structures can be obtained from the Fachinformationszentrum Karlsruhe, DE-76344 Eggenstein-Leopoldshafen, Germany, (fax: 49 7247 808 666; e-mail:crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD_413049 ($\text{Na}_2\text{S}_2\text{O}_7$) and CSD_413050 (KNaS_2O_7).

3. Discussion

The disulphate anions are essentially in the eclipsed configuration. Oxygens form close to regular tetrahedral

Table 1
Selected data collection and refinement parameters for $\text{K}_2\text{S}_2\text{O}_7$, KNaS_2O_7 and $\text{Na}_2\text{S}_2\text{O}_7$

Sample	$\text{K}_2\text{S}_2\text{O}_7$	KNaS_2O_7	$\text{Na}_2\text{S}_2\text{O}_7$	$\text{Na}_2\text{S}_2\text{O}_7$
Method	Powder	Powder	Powder	Single crystal
Wavelength (Å)	1.5226	1.5226	1.5226	0.71073
Temperature (K)	295(1)	295(1)	295(1)	120(1)
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	2	2	2
No. of Bragg reflections	375	657	591	1373
No. of parameters	36	64	92	100
R_p (%) / R_F (%)	14.9	14.2	17.0	3.30
wR_p (%) / wR_F^2 (%)	15.7	13.4	18.1	8.34
GOF	17.1	16.0	26.3	1.08
R_{Bragg} (%)	9.6	7.5	10.0	—
Unit cell				
a (Å)	12.3653(2)	5.90476(9)	6.8037(1)	6.7702(9)
b (Å)	7.3122(1)	7.2008(1)	6.8266(1)	6.7975(10)
c (Å)	7.2868(1)	7.4188(1)	6.7841(1)	6.7292(9)
α (°)	90.0	101.7074(9)	116.3599(9)	116.779(2)
β (°)	93.0792(7)	90.6960(9)	95.9555(9)	96.089(3)
γ (°)	90.0	94.2403(9)	84.1945(9)	84.000(3)
V (Å ³)	657.90(3)	307.91(2)	280.27(2)	274.35(7)
ρ (g/cm ³)	2.567	2.569	2.631	2.689
μ (cm ⁻¹)	181	141	97	11

Table 2a
Fractional coordinates and isotropic temperature factor coefficients for $\text{K}_2\text{S}_2\text{O}_7$ based on powder diffraction data (P): $C2/c$, $a = 12.3653(2)$, $b = 7.3122(1)$, $c = 7.2868(1)$ Å, $\beta = 93.0792(7)^\circ$

	x	y	z	B (Å ²)
K(1)	0.3551(1)	0.6545(2)	0.6440(2)	3.8(1)
S(1)	0.3961(2)	0.1838(3)	0.6389(3)	3.4(1)
O(1)	0.4390(3)	0.2826(6)	0.4921(6)	3.1(1)
O(2)	0.3572(3)	0.2950(6)	0.7751(6)	3.1
O(3)	0.3374(3)	0.0118(5)	0.5791(6)	3.1
O(4)	0.5000	0.0812(9)	0.7500	3.1

Table 2b

Fractional coordinates and isotropic temperature factor coefficients for KNaSO based on powder diffraction data (P): $P\bar{1}$, $a = 5.90476(9)$, $b = 7.2008(1)$, $c = 7.4188(1)\text{ }$, $\alpha = 101.7074(9)$, $\beta = 90.6960(9)$, $\gamma = 94.2403(9)^\circ$

	x	y	z	B ( ²)
K(1)	0.7723(4)	0.2221(3)	0.5731(3)	2.8(1)
Na(1)	0.2128(6)	0.6450(5)	0.8926(5)	2.8(1)
S(1)	0.7064(6)	0.7258(5)	0.6886(5)	4.8(1)
S(2)	0.2780(5)	0.1720(4)	0.9033(5)	3.3(1)
O(1)	0.4988(12)	0.6378(9)	0.6969(9)	4.4(2)
O(2)	0.8972(12)	0.6192(10)	0.6954(9)	5.9(2)
O(3)	0.7471(11)	0.8505(9)	0.5711(9)	5.7(2)
O(4)	0.7406(10)	0.8620(7)	0.9030(8)	3.1(2)
O(5)	0.2297(9)	0.9815(9)	0.7950(8)	2.7(2)
O(6)	0.5108(10)	0.2632(7)	0.8839(8)	2.4(2)
O(7)	0.0939(11)	0.3035(8)	0.8864(8)	2.8(2)

Table 2c

Fractional coordinates and isotropic average temperature factor coefficients for NaSO based on single-crystal data (S) at 120 K: $P\bar{1}$, $a = 6.7702(9)$, $b = 6.7975(10)$, $c = 6.7292(9)\text{ }$, $\alpha = 116.779(2)$, $\beta = 96.089(3)$, $\gamma = 84.000(3)^\circ$

	x	y	z	B _{ave} ( ²)
Na(1)	0.13493(16)	0.81885(18)	0.77174(17)	1.09(2)
Na(2)	0.66343(14)	0.75761(17)	0.38605(16)	0.79(2)
S(1)	0.15765(9)	0.74578(10)	0.26730(10)	0.56(1)
S(2)	0.3602(9)	0.31296(10)	0.13955(10)	0.57(1)
O(1)	0.0084(3)	-0.2948(3)	0.3801(3)	0.87(3)
O(2)	0.6754(3)	0.1519(3)	0.5817(3)	0.91(3)
O(3)	0.9177(3)	0.1517(3)	0.8731(3)	0.80(3)
O(4)	0.7583(2)	0.4899(3)	0.9148(3)	0.62(3)
O(5)	0.6401(3)	0.8625(3)	0.0835(3)	0.79(3)
O(6)	0.2413(3)	0.2864(3)	0.2894(3)	0.87(3)
O(7)	0.4463(2)	0.6074(3)	0.7653(3)	0.78(3)

arrangements. The volume distortion [16] of individual tetrahedra is only 1% or lower. S atoms are displaced from the centre of tetrahedron, making the bond to the bridging O4 atom significantly longer than the rest, with the exception of S2 in KNaS₂O₇ which lies very close to the centroid of its coordination. There are some differences between the three structures in the mutual position of the two tetrahedra in a disulphate group. This can be described by the two relative rotations of the tetrahedral groups: one in the plane defined by the two S atoms, O4, and the additional two oxygens lying approximately in the same plane, the other perpendicular to this plane. It can be seen (Table 3) that the S–O4–S angle, which describes the first rotation, is about 10° larger in KNaS₂O₇ than in the two other structures. On the other side, the other rotation is 13° in Na₂S₂O₇, while it is only 2° in K₂S₂O₇, and 1° in KNaS₂O₇. Like other eclipsed dianion structures, the alkali disulphates belong to the group of dichromate-like structures [17]. The alkali cations coordinate the disulphate oxygens so to form a three-dimensional network. All terminal disulphate oxygens are in this

way coordinated by at least two cations. While the bridging oxygen, O(4), in most eclipsed dianion structures is engaged in cation coordination [17], O(4) is not found in the first coordination sphere of cations in the disulphates.

The alkali elements in the three disulphates have many oxygen neighbours, and it is not straightforward to determine the coordination numbers as there is not always a consistent and large gap between the group of first and next neighbours. As seen for the K in KNaS₂O₇ which has the largest number of potentially bonded oxygens, the distances to the closest ten oxygens vary almost continuously from 2.67 to 3.47  (Table 3). To determine the bonding limits and the coordination numbers for the alkali ions, an analysis of the electron density distribution based on the procrystal model was undertaken. The calculation was done with our own computer program which uses the coefficients of atomic functions of [18]. The K ions in K₂S₂O₇ and KNaS₂O₇ share atom domain surfaces with nine and ten closest oxygens, respectively. However, the bond critical points and bond paths exist only to the closest seven and eight

Table 3
Selected interatomic distances (Å) and angles (deg.) for $K_2S_2O_7$, $KNaS_2O_7$ and $Na_2S_2O_7$

	$K_2S_2O_7$ (P)		$KNaS_2O_7$ (P)		$Na_2S_2O_7$ (S)	
S(1)–O(1)		1.417(5)		1.346(8)		1.443(2)
S(1)–O(2)		1.389(5)		1.416(8)		1.441(2)
S(1)–O(3)		1.505(4)		1.383(8)		1.434(2)
S(1)–O(4)		1.660(4)		1.692(7)		1.606(2)
S(2)–O(4)				1.510(7)		1.652(2)
S(2)–O(5)				1.449(7)		1.436(2)
S(2)–O(6)				1.500(6)		1.438(2)
S(2)–O(7)				1.514(7)		1.439(2)
O(1)–S(1)–O(2)		113.5(3)		117.9(5)		111.5(1)
O(1)–S(1)–O(3)		113.7(3)		121.1(5)		114.8(1)
O(1)–S(1)–O(4)		106.7(2)		101.6(4)		107.4(1)
O(2)–S(1)–O(3)		121.0(3)		109.6(4)		114.6(1)
O(2)–S(1)–O(4)		101.8(2)		97.2(4)		106.6(1)
O(3)–S(1)–O(4)		96.5(3)		105.0(4)		100.7(1)
O(5)–S(2)–O(6)				115.8(4)		115.9(1)
O(5)–S(2)–O(7)				113.3(4)		114.5(1)
O(5)–S(2)–O(4)				101.6(3)		98.8(1)
O(6)–S(2)–O(7)				112.1(4)		114.5(1)
O(6)–S(2)–O(4)				108.3(4)		105.7(1)
O(7)–S(2)–O(4)				104.4(4)		105.0(1)
S(1)–O(4)–S(1)/S(2)		126.3(4)		135.6(4)		125.7(1)
K(1)/Na(1)–	O(3)	2.662(4)	O(3)	2.667(7)	O(3)	2.369(2)
K(1)/Na(1)–	O(1)	2.728(4)	O(6)	2.769(6)	O(7)	2.417(2)
K(1)/Na(1)–	O(2)	2.714(4)	O(5)	2.825(6)	O(3)	2.424(2)
K(1)/Na(1)–	O(2)	2.797(4)	O(2)	2.856(7)	O(1)	2.470(2)
K(1)/Na(1)–	O(1)	2.820(4)	O(7)	2.920(6)	O(5)	2.536(2)
K(1)/Na(1)–	O(2)	2.908(4)	O(1)	2.927(7)	O(6)	2.658(2)
K(1)/Na(1)–	O(3)	3.061(4)	O(3)	3.088(7)	O(2)	2.911(2)
K(1)/Na(1)–	O(1)	3.134(4)	O(2)	3.126(7)		
K(1)/Na(1)–	O(3)	3.367(4)	O(3)	3.206(7)		
			O(1)	3.471(7)		
Na(1)/Na(2)–			O(1)	2.237(8)	O(2)	2.319(2)
Na(1)/Na(2)–			O(6)	2.276(7)	O(1)	2.327(2)
Na(1)/Na(2)–			O(2)	2.328(8)	O(6)	2.350(2)
Na(1)/Na(2)–			O(7)	2.456(7)	O(7)	2.386(2)
Na(1)/Na(2)–			O(7)	2.499(7)	O(2)	2.401(2)
Na(1)/Na(2)–			O(5)	2.661(7)	O(5)	2.428(2)
Na(1)/Na(2)–					O(4)	2.961(2)

All K–O and Na–O distances less than 3.5 Å and 3.0 Å, respectively are shown. K–O and Na–O distances in bold faces are considered part of the coordination sphere.

oxygens, respectively. As seen from the coordination characteristics calculated for different coordination numbers (Table 4), these characteristics also support 7 and 8 as the coordination numbers of K in $K_2S_2O_7$ and $KNaS_2O_7$, respectively, because they have the largest sphericities (SPH) of coordinations. Sphericities are reciprocal to the deviations of vertices of a coordination polyhedron from a common sphere, and vary, according to the definition, between 0 and 1, 1 being the ideal sphericity [19]. In $KNaS_2O_7$, Na has direct contact to only six oxygens. The atomic domain of Na(1) in $Na_2S_2O_7$ shares surfaces to eight closest oxygens, while Na(2) has seven such neighbours. However, in all these

cases the bond critical points can be found only to the closest six oxygens. As for K, the values of coordination sphericities (SPH) also suggest 6 as the coordination number for all three coordinations. There are important variations between the coordinations of the alkali ions in the three disulphates. As expected, K shows larger average bond distances, radii of circumscribed spheres (r_s) and volumes of coordination polyhedra (V_p) than Na. However, there are systematic variations between coordinations of the same element in the different disulphates. Although the same coordination number can be chosen for Na for the three different sites it occupies, they show significantly different characteris-

Table 4
Alkali ion coordination characteristics

Site	Compound	CN	Average bond length (Å)	r_s (Å)	V_P (Å ³)	v	SPH	ECC
K	K ₂ S ₂ O ₇	9	2.91 (0.23)	2.89	44.85(1)	0.087	0.942	0.097
K	K ₂ S ₂ O ₇	8	2.86 (0.17)	2.84	38.11(1)	0.084	0.959	0.076
K	K ₂ S ₂ O ₇	7	2.82 (0.15)	2.81	31.41(1)	0.111	0.964	0.064
K	KNaS ₂ O ₇	10	2.96 (0.24)	2.96	53.61(2)	0.076	0.934	0.089
K	KNaS ₂ O ₇	9	2.93 (0.18)	2.92	46.48(2)	0.084	0.948	0.054
K	KNaS ₂ O ₇	8	2.90 (0.15)	2.86	38.91(2)	0.086	0.974	0.079
K	KNaS ₂ O ₇	7	2.86 (0.13)	2.85	33.06(2)	0.104	0.973	0.071
Na	KNaS ₂ O ₇	6	2.41 (0.16)	2.40	17.58(1)	0.049	0.943	0.059
Na(1)	Na ₂ S ₂ O ₇	8	2.66 (0.37)	2.66	31.58(5)	0.075	0.886	0.165
Na(1)	Na ₂ S ₂ O ₇	7	2.54 (0.19)	2.52	22.32(4)	0.125	0.939	0.074
Na(1)	Na ₂ S ₂ O ₇	6	2.48 (0.10)	2.47	17.49(3)	0.134	0.962	0.027
Na(2)	Na ₂ S ₂ O ₇	7	2.46 (0.22)	2.44	21.22(4)	0.081	0.935	0.109
Na(2)	Na ₂ S ₂ O ₇	6	2.38 (0.04)	2.38	17.11(3)	0.047	0.990	0.021

r_s is the radius of circumscribed sphere, V_P the volume of coordination polyhedron, v the volume deformation, SPH the sphericity and ECC the eccentricity. The parameters are calculated by the program IVTON [20]. For the method of calculation see [16,19].

tics. It can be noted in Na₂S₂O₇ that the coordination of Na(1) has both a larger size and a larger volume distortion (v) than Na(2), although their sphericities are almost equal, and the eccentricity of the central atom in coordination (ECC) is even somewhat smaller for the former. The two sites have therefore distinctly different characteristics, with Na(1) being surrounded by a larger and more distorted coordination. This resembles the situation in KNaS₂O₇, with Na(2) resembling the Na coordination, while Na(1) corresponds to that of K. It should also be noted that a presence of both elements in the same structure emphasises the differences between the coordinations, and Na coordination in KNaS₂O₇ is the smallest of the three Na coordinations, while that of K is larger and even with a higher coordination number than the unique K coordination in K₂S₂O₇.

All the three crystal structures can be described as built from the same type of infinite chains. Within a chain the disulphates are turned in the same direction and linked via two cations to the next disulphate (Fig. 2). The differences between the structures lie in the way the chains are connected through further cation coordinations. Expanding the structures in the plane of the chains into sheets, the chains are parallel in KNaS₂O₇, while in K₂S₂O₇ and Na₂S₂O₇ they are antiparallel with the chain directions alternating (Fig. 2). In KNaS₂O₇ and K₂S₂O₇ the chains are connected on both sides by cation coordinations within a sheet, while in Na₂S₂O₇ the chains are connected pair-wise only. The sheets are parallel to $\{-101\}$ in K₂S₂O₇, to $\{100\}$ in KNaS₂O₇, and to $\{210\}$ in Na₂S₂O₇. The sheets are then stacked with every second sheet inverted, in accordance with the centres of symmetry, allowing for cross-linking cation–oxygen coordinations. In K₂S₂O₇ and Na₂S₂O₇, it results in a step-like arrangement of the disulphate groups, while in KNaS₂O₇ they are stacked on top of

each other (Fig. 3). Again there is a slight difference between the K₂S₂O₇ and Na₂S₂O₇ structures: While K₂S₂O₇ sheets appear highly planar; the Na₂S₂O₇ sheets are slightly corrugated to allow for shorter cation oxygen distances.

When viewing the packing of K and Na polyhedra (Fig. 3) the differences between the structures can be described as follows: In K₂S₂O₇ the K coordination polyhedra from neighbouring chains in the same sheet share square faces, while they share an edge with the K polyhedron from the same chain (Fig. 3a). In this way, wavy columns of K coordination polyhedra are formed along $[101]$. In KNaS₂O₇ the K and Na coordination polyhedra from neighbouring chains in a sheet share a common triangular face, while the two belonging to the same chain share an edge. The polyhedral columns formed in this way run along $[001]$ (Fig. 3b). K polyhedra, which are slightly deformed square antiprisms with bases parallel to (210) and inclined to the plane of the sheets, share also an edge with a K polyhedron from one of the neighbouring sheets. Na octahedra share also an edge with a neighbouring Na octahedron from the same sheet. With these interconnections zig-zag columns of edge-sharing antiprisms of K are formed along $[010]$, underlied and overlid by pairs of edge-sharing Na octahedra. Generally, the K and Na coordinations are arranged on different levels parallel to $\{001\}$ and perpendicular to the elongation of the disulphate groups. Due to smaller coordination polyhedra of Na and their different orientation, in the structure of Na₂S₂O₇ the polyhedral columns of another type are formed (Fig. 3c). The coordination octahedra of Na share only a vertex with the neighbouring Na coordination from the same disulphate–Na chain, while they share an edge with the Na polyhedra from neighbouring chains. This edge is nearly parallel to the

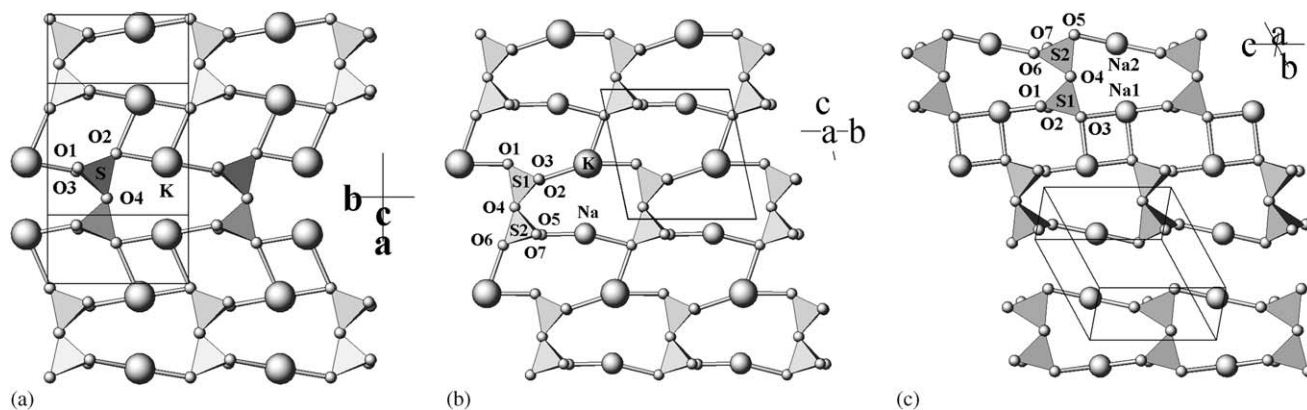


Fig. 2. Single layers of (a) $K_2S_2O_7$, (b) $KNaS_2O_7$ and (c) $Na_2S_2O_7$. The common chain structure runs horizontally. Disulphate groups are shown as tetrahedral, large spheres are K, intermediate spheres Na and small spheres O.

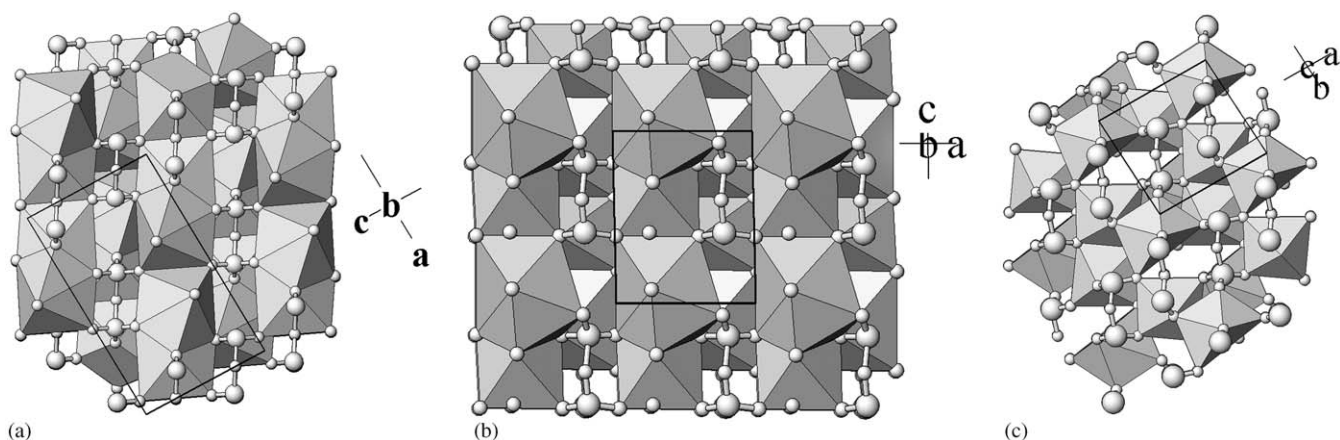


Fig. 3. Perspective drawings of the cation coordination polyhedra in (a) $K_2S_2O_7$, (b) $KNaS_2O_7$ and (c) $Na_2S_2O_7$. Large spheres are S and small spheres O.

plane of the sheet in the case of Na1–Na1 contact, while it is nearly perpendicular to it in the case of Na2–Na2 contact. In this way, wavy columns of the edge-sharing octahedra are formed along the [101] direction. In this case, the columns run perpendicular to the elongation direction of the disulphate groups, and not parallel to them like in the case of $K_2S_2O_7$ or $KNaS_2O_7$.

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