

An unexpected oxidation:  $\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$  revisited

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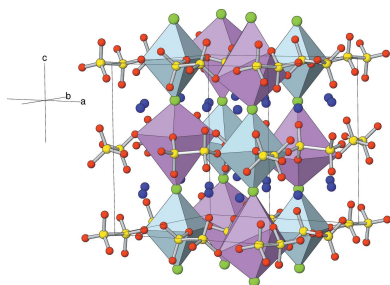
The title compound,  $\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$  [systematic name: sodium pentapotassium dichloride bis(dithionate)], arose as an unexpected product from an organic synthesis that used dithionite ( $\text{S}_2\text{O}_4^{2-}$ ) ions as a reducing agent to destroy excess permanganate ions. Compared to the previous study [Stanley (1953). *Acta Cryst.* **6**, 187–196], the present tetragonal structure exhibits a  $\sqrt{2}a \times \sqrt{2}a \times c$  supercell due to subtle changes in the orientations of the dithionate anions. The structure can be visualized as a three-dimensional framework of [001] columns of alternating *trans*- $\text{NaO}_4\text{Cl}_2$  and  $\text{KO}_4\text{Cl}_2$  octahedra cross-linked by the dithionate ions with the interstices occupied by  $\text{KO}_6\text{Cl}_2$  polyhedra to generate a densely packed three-dimensional framework. The asymmetric unit comprises two sodium ions (site symmetries 4 and  $\bar{4}$ ), four potassium ions (site symmetries =  $\bar{4}$ , 4, 1 and 1), three chloride ions (site symmetries = 4, 4 and 2) and two half-dithionate ions (all atoms on general positions). Both dithionate ions are completed by crystallographic inversion symmetry. The crystal chosen for data collection was found to be rotationally twinned by  $180^\circ$  about the [100] axis in reciprocal space with a 0.6298 (13):0.3702 (13) domain ratio.

## 1. Chemical context

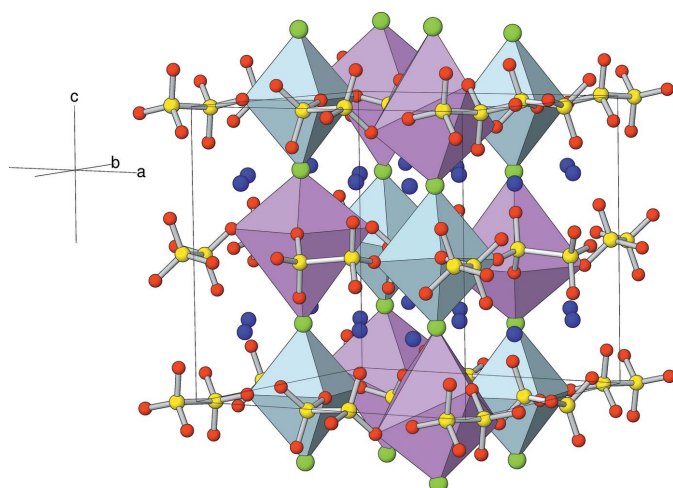
As well as their large-scale industrial use in reducing and solubilizing vat dyes such as indigo (Božič & Kokol, 2008), dithionites containing the  $\text{S}_2\text{O}_4^{2-}$  anion (sulfur oxidation state = +3) have long found use as moderately strong reducing agents in organic synthesis (De Vries & Kellogg, 1980, and references therein). The title mixed-cation, mixed-anion compound,  $\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$  (I), containing  $\text{S}_2\text{O}_6^{2-}$  dithionate ions (sulfur oxidation state = +5), arose as a completely unexpected side product from an attempt to oxidize hexamethyl benzene to mellitic acid as a precursor of synthetic mellite (Plater & Harrison, 2015): sodium dithionite was added to the reaction to destroy excess permanganate ions (as  $\text{KMnO}_4$ ) and the source of the chloride ions was added HCl. To our slight surprise, the structure of the title compound, along with that of the non-isostructural  $\text{Na}_2\text{K}_4\text{Cl}_2(\text{S}_2\text{O}_6)_2$ , was established over 60 years ago (Stanley, 1953). This re-determination presents a superstructure of the earlier reported structure, which arises from subtle orientational changes for the dithionate anions.

## 2. Structural commentary

Compound (I) comprises two sodium ions (Na1 site symmetry = 4, Na2 site symmetry =  $\bar{4}$ ), four potassium ions (site symmetries =  $\bar{4}$ , 4, 1 and 1 for K1, K2, K3 and K4, respectively), three chloride ions (Cl1 and Cl2 with site symmetry 4, Cl3 with site symmetry 2) and two half-dithionate ions (all atoms on general positions) in the asymmetric unit. Selected







**Figure 4**  
Polyhedral view of the structure of (I), showing the [001] chains of  $\text{NaO}_4\text{Cl}_2$  octahedra (blue) and  $\text{KO}_4\text{Cl}_2$  (K1 and K2) octahedra (lilac) cross-linked by the dithionate groups. Atoms K3 and K4 are shown as purple spheres.

thionate ion and the Na1 and K1 cations reside (Fig. 1); at  $z \sim 1/2$ , are to be found the S2/O4/O5/O6 dithionate ion and Na2 and K2 (Fig. 2). Between them, at  $z \sim 1/4$  and  $3/4$ , are K3, K4 and the three chloride ions, which form a distorted square grid (Fig. 3).

The extended structure of (I) can be visualized (Fig. 4) as [001] chains of alternating *trans*- $\text{NaO}_4\text{Cl}_2$  and  $\text{KO}_4\text{Cl}_2$  octahedra linked *via* their chloride ions and cross-linked by the dithionate groups. There are two distinct chains: the Na1 and K2 species and their linking chloride ions (Cl1 and Cl2) lie on the fourfold axes at  $(1/4, 1/4, z)$  and  $(3/4, 3/4, z)$ , whereas Na2 and K1 (both site symmetry  $\bar{4}$ ) are connected by Cl3, which lies on the  $(1/4, 3/4, z)$  twofold axis and its symmetry-generated clone at  $(3/4, 1/4, z)$ . As expected, the Na–O bonds (mean = 2.34 Å) are much shorter than the K–O bonds (mean = 2.82 Å). In terms of bond angles, the sodium-centred octahedra are almost regular [spread of *cis* and *trans* bond angles = 87.94 (4)–92.06 (4) and 175.89 (8)–180°, respectively, for Na1 and 86.02 (3)–93.98 (3) and 172.03 (5)–180°, respectively, for Na2] but the potassium-centred moieties are grossly distorted with ranges of *cis* and *trans* angles of 71.75 (2)–108.25 (2) and 143.50 (4)–180°, respectively, for K1 and 74.91 (2)–105.09 (2) and 149.82 (5)–180°, respectively, for K2.

The structure of (I) is completed by the K3 and K4 potassium ions, which occupy interstices in the framework described in the preceding paragraph. The K3 coordination polyhedron approximates to an extremely distorted  $\text{KO}_6\text{Cl}_2$  square anti-prism. The coordination for K4 is slightly ambiguous, with six shorter K–O bonds [2.8429 (11)–3.0664 (12) Å] and two K–Cl links [3.1168 (5) and 3.1291 (5) Å] forming a squashed and distorted square anti-prism. There are two further  $\text{K4} \cdots \text{O}$  close contacts at 3.2273 (12) and 3.3822 (12) Å [the next-nearest  $\text{K4} \cdots \text{O}$  separation after these is 4.3935 (13) Å] but given that these  $\text{K4} \cdots \text{O}$  contacts are longer than the K4–Cl bonds and have bond valences (Brown & Altermatt, 1985) of less than 0.05 (Brown, 2002), we regard

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$
$M_r$	609.63
Crystal system, space group	Tetragonal, $P4/n$
Temperature (K)	100
$a, c$ (Å)	12.0421 (1), 11.3925 (2)
$V$ (Å <sup>3</sup> )	1652.05 (4)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	2.24
Crystal size (mm)	$0.05 \times 0.02 \times 0.02$
Data collection	
Diffractometer	Rigaku Mercury CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2004)
$T_{\min}$ , $T_{\max}$	0.911, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	1910, 1910, 1834
$(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , $S$	0.015, 0.043, 1.06
No. of reflections	1910
No. of parameters	113
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.35, -0.35

Computer programs: *CrystalClear* (Rigaku, 2010), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Dowty, 1999).

them as not significant. The three chloride ions each adopt almost regular  $\text{ClK}_5\text{Na}$  octahedral geometries.

Bond-valence sum (BVS) data (Brown & Altermatt, 1985) for the cations in (I) indicate that the sodium ions in (I) are considerably ‘overbonded’:  $\text{BVS}(\text{Na1}) = 1.46$  and  $\text{BVS}(\text{Na2}) = 1.45$  (expected value = 1.0 valence units). Three of the potassium ions are possibly slightly over-bonded (BVS values for K1, K2 and K3 = 1.16, 1.19 and 1.19, respectively) whereas K4 (BVS = 1.01) achieves its expected valence almost exactly.

The previously-reported structure of  $\text{NaK}_5\text{Cl}_2(\text{S}_2\text{O}_6)_2$  (Stanley, 1953) was modelled in space group  $P4/mnc$  [ $a_S = 8.5621$  (6),  $c_S = 11.5288$  (6) Å,  $V_S = 845.2$  Å<sup>3</sup>; S = Stanley], thus it may be seen that the present unit cell is a  $\sqrt{2}a_S \times \sqrt{2}a_S \times c_S$  super-cell of the Stanley structure with doubled volume. The relative dispositions of the sodium, potassium and chloride ions in the Stanley structure are almost the same as in (I); the main difference occurs in the orientation of the dithionate ions with respect to the (001) plane; in the Stanley structure, this species, which is built up from one unique S atom and two unique O atoms, has  $2/m$  ( $C_{2h}$ ) point-group symmetry about the mid-point of the S–S bond with the S atom and one of the O atoms lying on the  $z = 0$  mirror plane [compare the deviations from the (001) plane noted above for the S1–O1 and S2–O5 bonds in (I)].

### 3. Database survey

As already noted, this structure (ICSD reference number 24676) was previously reported by Stanley (1953). A survey of the Cambridge Structural Database (Groom *et al.*, 2016)

(entries updated to 20 December 2016) revealed 138 crystal structures containing dithionate anions.

#### 4. Synthesis and crystallization

In an attempt to prepare mellitic acid ( $C_6H_6O_{12}$ ) as a precursor of synthetic mellite (Plater & Harrison, 2015), hexamethylbenzene (2.0 g, 0.0123 moles) and  $KMnO_4$  (23.4 g, 0.148 moles, 12 equiv.) were refluxed in water for 24 h (Friedel & Crafts, 1884): the organic starting material had a tendency to sublime into the condenser. After cooling, the mixture was treated with excess  $Na_2S_2O_4$  to decompose the unreacted permanganate, which turned the solution brown. It was filtered and then treated with conc. HCl to give a pH of 1. After leaving to crystallize, the solid product (1.34 g) was collected by filtration as colourless blocks of (I). Evidently, dithionite has been oxidized by permanganate to dithionate by an unknown pathway and the sodium and potassium cations and chloride ions (from the hydrochloric acid) present in the mixture serendipitously combine with the dithionate ions to form (I).

#### 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the atoms in the asymmetric unit were located by *SHELXT* (Sheldrick, 2015a): the potassium cations and chloride anions were distinguished in terms

of chemically reasonable environments. The crystal chosen for data collection was found to be rotationally twinned by  $180^\circ$  about the [100] axis in reciprocal space with a 0.6298 (13):0.3702 (13) domain ratio.

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## supporting information

*Acta Cryst.* (2017). E73, 188-191 [https://doi.org/10.1107/S2056989017000494]

An unexpected oxidation: NaK<sub>5</sub>Cl<sub>2</sub>(S<sub>2</sub>O<sub>6</sub>)<sub>2</sub> revisited

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## Computing details

Data collection: *CrystalClear* (Rigaku, 2010); cell refinement: *CrystalClear* (Rigaku, 2010); data reduction: *CrystalClear* (Rigaku, 2010); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

## Sodium pentapotassium dichloride bis(dithionate)

*Crystal data*

NaK<sub>5</sub>Cl<sub>2</sub>(S<sub>2</sub>O<sub>6</sub>)<sub>2</sub>  
 $M_r = 609.63$   
 Tetragonal, *P4/n*  
 $a = 12.0421$  (1) Å  
 $c = 11.3925$  (2) Å  
 $V = 1652.05$  (4) Å<sup>3</sup>  
 $Z = 4$   
 $F(000) = 1200$

$D_x = 2.451$  Mg m<sup>-3</sup>  
 Mo *K*α radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 23162 reflections  
 $\theta = 2.3$ – $27.5^\circ$   
 $\mu = 2.24$  mm<sup>-1</sup>  
 $T = 100$  K  
 Block, colourless  
 $0.05 \times 0.02 \times 0.02$  mm

*Data collection*

Rigaku Mercury CCD  
 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 2004)  
 $T_{\min} = 0.911$ ,  $T_{\max} = 1.000$   
 1910 measured reflections

1910 independent reflections  
 1834 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 27.5^\circ$ ,  $\theta_{\min} = 1.8^\circ$   
 $h = -10 \rightarrow 11$   
 $k = -15 \rightarrow 15$   
 $l = -14 \rightarrow 14$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.015$   
 $wR(F^2) = 0.043$   
 $S = 1.06$   
 1910 reflections  
 113 parameters  
 0 restraints

Primary atom site location: structure-invariant  
 direct methods  
 $w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 0.4886P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.35$  e Å<sup>-3</sup>

*Special details*

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Refinement.** Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Na1	0.2500	0.2500	0.01268 (9)	0.0094 (3)
Na2	0.7500	0.2500	0.5000	0.0084 (3)
K1	0.7500	0.2500	0.0000	0.01621 (19)
K2	0.2500	0.2500	0.51306 (5)	0.01506 (18)
K3	0.50130 (4)	0.19113 (2)	0.24632 (3)	0.01042 (8)
K4	0.18440 (2)	0.00129 (4)	0.74572 (3)	0.01187 (8)
S1	0.51535 (4)	0.58649 (4)	0.00758 (3)	0.00962 (10)
O1	0.63276 (11)	0.59544 (11)	−0.02005 (10)	0.0160 (3)
O2	0.48827 (9)	0.61202 (9)	0.12870 (9)	0.0163 (2)
O3	0.44243 (10)	0.63754 (9)	−0.07768 (9)	0.0190 (2)
S2	0.08586 (4)	0.51687 (4)	0.49086 (3)	0.00872 (10)
O4	0.10996 (9)	0.48723 (9)	0.37002 (9)	0.0152 (2)
O5	0.09283 (11)	0.63505 (10)	0.51433 (9)	0.0142 (3)
O6	0.13966 (9)	0.44729 (9)	0.57748 (9)	0.0169 (2)
Cl1	0.2500	0.2500	0.77619 (6)	0.00944 (14)
Cl2	0.2500	0.2500	0.25196 (5)	0.00958 (16)
Cl3	0.2500	0.7500	0.26312 (4)	0.00951 (13)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
K1	0.0200 (3)	0.0200 (3)	0.0086 (3)	0.000	0.000	0.000
K2	0.0183 (3)	0.0183 (3)	0.0086 (3)	0.000	0.000	0.000
K3	0.00940 (15)	0.01049 (13)	0.01136 (15)	0.00021 (17)	0.00028 (9)	−0.00154 (12)
K4	0.01177 (13)	0.00978 (15)	0.01406 (15)	−0.00037 (17)	−0.00130 (13)	0.00016 (10)
Na1	0.0094 (5)	0.0094 (5)	0.0095 (5)	0.000	0.000	0.000
Na2	0.0080 (5)	0.0080 (5)	0.0090 (5)	0.000	0.000	0.000
S1	0.0104 (2)	0.0092 (2)	0.00920 (16)	−0.00190 (19)	0.00093 (11)	−0.00018 (12)
O1	0.0137 (7)	0.0134 (6)	0.0208 (5)	−0.0041 (6)	0.0057 (4)	−0.0037 (5)
O2	0.0201 (6)	0.0156 (5)	0.0131 (5)	−0.0047 (5)	0.0054 (5)	−0.0053 (4)
O3	0.0211 (6)	0.0137 (5)	0.0223 (6)	−0.0004 (5)	−0.0074 (5)	0.0047 (5)
S2	0.0080 (2)	0.0088 (2)	0.00928 (16)	−0.00075 (18)	0.00053 (12)	−0.00015 (12)
O4	0.0139 (5)	0.0188 (6)	0.0129 (5)	−0.0036 (5)	0.0053 (4)	−0.0044 (4)
O5	0.0134 (7)	0.0091 (6)	0.0200 (5)	−0.0031 (5)	0.0024 (4)	−0.0026 (4)
O6	0.0129 (5)	0.0176 (6)	0.0202 (5)	−0.0001 (5)	−0.0040 (4)	0.0061 (5)
Cl1	0.0100 (2)	0.0100 (2)	0.0084 (3)	0.000	0.000	0.000
Cl2	0.0099 (2)	0.0099 (2)	0.0090 (3)	0.000	0.000	0.000
Cl3	0.0107 (3)	0.0093 (2)	0.0085 (2)	0.00012 (15)	0.000	0.000

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Na1—O1 <sup>i</sup>	2.3375 (13)	K4—O5 <sup>xiv</sup>	3.2273 (12)
Na1—O1 <sup>ii</sup>	2.3375 (13)	K4—O1 <sup>xvi</sup>	3.3822 (12)
Na1—O1 <sup>iii</sup>	2.3375 (13)	S1—O3	1.4465 (11)
Na1—O1 <sup>iv</sup>	2.3375 (13)	S1—O2	1.4507 (10)
Na1—Cl1 <sup>v</sup>	2.6942 (13)	S1—O1	1.4526 (13)
Na1—Cl2	2.7260 (12)	S1—S1 <sup>i</sup>	2.1227 (9)
Na2—O5 <sup>vi</sup>	2.3506 (13)	O1—Na1 <sup>i</sup>	2.3375 (13)
Na2—O5 <sup>vii</sup>	2.3506 (13)	O1—K3 <sup>xvii</sup>	2.9148 (11)
Na2—O5 <sup>viii</sup>	2.3506 (13)	O1—K4 <sup>xviii</sup>	3.3822 (12)
Na2—O5 <sup>ix</sup>	2.3506 (13)	O2—K4 <sup>xix</sup>	2.8429 (11)
Na2—Cl3 <sup>ix</sup>	2.6986 (5)	O2—K3 <sup>xi</sup>	2.8705 (11)
Na2—Cl3 <sup>vii</sup>	2.6986 (5)	O2—K4 <sup>xviii</sup>	3.0664 (12)
K1—O3 <sup>viii</sup>	2.8262 (12)	O3—K1 <sup>i</sup>	2.8262 (12)
K1—O3 <sup>ix</sup>	2.8262 (12)	O3—K3 <sup>i</sup>	2.8995 (11)
K1—O3 <sup>x</sup>	2.8262 (12)	O3—K4 <sup>xx</sup>	3.0290 (11)
K1—O3 <sup>i</sup>	2.8262 (12)	S2—O6	1.4475 (11)
K1—Cl3 <sup>ix</sup>	2.9976 (5)	S2—O5	1.4505 (13)
K1—Cl3 <sup>i</sup>	2.9976 (5)	S2—O4	1.4516 (10)
K2—O6	2.8193 (11)	S2—S2 <sup>xxi</sup>	2.1176 (9)
K2—O6 <sup>viii</sup>	2.8193 (12)	O4—K3 <sup>xi</sup>	2.7843 (11)
K2—O6 <sup>xi</sup>	2.8193 (12)	O4—K3 <sup>xii</sup>	2.8973 (11)
K2—O6 <sup>xii</sup>	2.8193 (11)	O4—K4 <sup>xxii</sup>	3.0284 (12)
K2—Cl2	2.9746 (8)	O5—Na2 <sup>vii</sup>	2.3506 (13)
K2—Cl1	2.9978 (9)	O5—K3 <sup>xxiii</sup>	3.0176 (11)
K3—O4 <sup>viii</sup>	2.7843 (11)	O5—K4 <sup>xxii</sup>	3.2273 (12)
K3—O2 <sup>viii</sup>	2.8705 (11)	O6—K4 <sup>xii</sup>	2.9235 (11)
K3—O4 <sup>xii</sup>	2.8973 (11)	O6—K4 <sup>viii</sup>	2.9941 (11)
K3—O3 <sup>i</sup>	2.8995 (11)	Cl1—Na1 <sup>xxiv</sup>	2.6943 (13)
K3—O1 <sup>iii</sup>	2.9148 (11)	Cl1—K4 <sup>xii</sup>	3.1168 (5)
K3—O5 <sup>vi</sup>	3.0176 (11)	Cl1—K4 <sup>viii</sup>	3.1168 (5)
K3—Cl3 <sup>ix</sup>	3.0836 (5)	Cl1—K4 <sup>xi</sup>	3.1168 (5)
K3—Cl2	3.1088 (5)	Cl2—K3 <sup>viii</sup>	3.1088 (5)
K4—O2 <sup>xiii</sup>	2.8429 (11)	Cl2—K3 <sup>xi</sup>	3.1088 (5)
K4—O6 <sup>xii</sup>	2.9235 (11)	Cl2—K3 <sup>xii</sup>	3.1088 (5)
K4—O6 <sup>xi</sup>	2.9941 (11)	Cl3—Na2 <sup>vii</sup>	2.6987 (5)
K4—O4 <sup>xiv</sup>	3.0284 (12)	Cl3—K1 <sup>i</sup>	2.9976 (5)
K4—O3 <sup>xv</sup>	3.0290 (11)	Cl3—K3 <sup>xi</sup>	3.0835 (5)
K4—O2 <sup>xvi</sup>	3.0664 (12)	Cl3—K3 <sup>xxv</sup>	3.0835 (5)
K4—Cl1	3.1168 (5)	Cl3—K4 <sup>xxii</sup>	3.1291 (5)
K4—Cl3 <sup>xiv</sup>	3.1291 (5)	Cl3—K4 <sup>xix</sup>	3.1291 (5)
O1 <sup>i</sup> —Na1—O1 <sup>ii</sup>	175.89 (8)	O6 <sup>xii</sup> —K4—Cl3 <sup>xiv</sup>	90.04 (2)
O1 <sup>i</sup> —Na1—O1 <sup>iii</sup>	89.926 (3)	O6 <sup>xi</sup> —K4—Cl3 <sup>xiv</sup>	130.64 (2)
O1 <sup>ii</sup> —Na1—O1 <sup>iii</sup>	89.926 (3)	O4 <sup>xiv</sup> —K4—Cl3 <sup>xiv</sup>	75.88 (2)
O1 <sup>i</sup> —Na1—O1 <sup>iv</sup>	89.926 (3)	O3 <sup>xv</sup> —K4—Cl3 <sup>xiv</sup>	67.35 (2)
O1 <sup>ii</sup> —Na1—O1 <sup>iv</sup>	89.926 (3)	O2 <sup>xvi</sup> —K4—Cl3 <sup>xiv</sup>	129.05 (2)

O1 <sup>iii</sup> —Na1—O1 <sup>iv</sup>	175.89 (8)	C11—K4—C13 <sup>xiv</sup>	150.327 (9)
O1 <sup>i</sup> —Na1—C11 <sup>v</sup>	92.06 (4)	O2 <sup>xiii</sup> —K4—O5 <sup>xiv</sup>	126.97 (3)
O1 <sup>ii</sup> —Na1—C11 <sup>v</sup>	92.06 (4)	O6 <sup>xii</sup> —K4—O5 <sup>xiv</sup>	66.79 (3)
O1 <sup>iii</sup> —Na1—C11 <sup>v</sup>	92.06 (4)	O6 <sup>xi</sup> —K4—O5 <sup>xiv</sup>	60.67 (3)
O1 <sup>iv</sup> —Na1—C11 <sup>v</sup>	92.06 (4)	O4 <sup>xiv</sup> —K4—O5 <sup>xiv</sup>	45.62 (3)
O1 <sup>i</sup> —Na1—C12	87.94 (4)	O3 <sup>xv</sup> —K4—O5 <sup>xiv</sup>	108.85 (3)
O1 <sup>ii</sup> —Na1—C12	87.94 (4)	O2 <sup>xvi</sup> —K4—O5 <sup>xiv</sup>	116.05 (3)
O1 <sup>iii</sup> —Na1—C12	87.94 (4)	C11—K4—O5 <sup>xiv</sup>	119.10 (3)
O1 <sup>iv</sup> —Na1—C12	87.94 (4)	C13 <sup>xiv</sup> —K4—O5 <sup>xiv</sup>	71.17 (3)
C11 <sup>v</sup> —Na1—C12	180.0	O2 <sup>xiii</sup> —K4—O1 <sup>xvi</sup>	73.26 (3)
O5 <sup>vi</sup> —Na2—O5 <sup>vii</sup>	172.03 (5)	O6 <sup>xii</sup> —K4—O1 <sup>xvi</sup>	131.92 (3)
O5 <sup>vi</sup> —Na2—O5 <sup>viii</sup>	90.277 (4)	O6 <sup>xi</sup> —K4—O1 <sup>xvi</sup>	107.92 (3)
O5 <sup>vii</sup> —Na2—O5 <sup>viii</sup>	90.277 (4)	O4 <sup>xiv</sup> —K4—O1 <sup>xvi</sup>	113.99 (3)
O5 <sup>vi</sup> —Na2—O5 <sup>ix</sup>	90.277 (4)	O3 <sup>xv</sup> —K4—O1 <sup>xvi</sup>	58.57 (3)
O5 <sup>vii</sup> —Na2—O5 <sup>ix</sup>	90.277 (4)	O2 <sup>xvi</sup> —K4—O1 <sup>xvi</sup>	44.07 (3)
O5 <sup>viii</sup> —Na2—O5 <sup>ix</sup>	172.03 (5)	C11—K4—O1 <sup>xvi</sup>	67.76 (3)
O5 <sup>vi</sup> —Na2—C13 <sup>ix</sup>	86.02 (3)	C13 <sup>xiv</sup> —K4—O1 <sup>xvi</sup>	113.60 (2)
O5 <sup>vii</sup> —Na2—C13 <sup>ix</sup>	86.02 (3)	O5 <sup>xiv</sup> —K4—O1 <sup>xvi</sup>	158.77 (2)
O5 <sup>viii</sup> —Na2—C13 <sup>ix</sup>	93.98 (3)	O3—S1—O2	114.34 (7)
O5 <sup>ix</sup> —Na2—C13 <sup>ix</sup>	93.98 (3)	O3—S1—O1	114.44 (7)
O5 <sup>vi</sup> —Na2—C13 <sup>vii</sup>	93.98 (3)	O2—S1—O1	114.16 (7)
O5 <sup>vii</sup> —Na2—C13 <sup>vii</sup>	93.98 (3)	O3—S1—S1 <sup>i</sup>	104.87 (6)
O5 <sup>viii</sup> —Na2—C13 <sup>vii</sup>	86.02 (3)	O2—S1—S1 <sup>i</sup>	104.25 (5)
O5 <sup>ix</sup> —Na2—C13 <sup>vii</sup>	86.02 (3)	O1—S1—S1 <sup>i</sup>	102.99 (6)
C13 <sup>ix</sup> —Na2—C13 <sup>vii</sup>	180.0	S1—O1—Na1 <sup>i</sup>	129.73 (8)
O3 <sup>viii</sup> —K1—O3 <sup>ix</sup>	143.50 (4)	S1—O1—K3 <sup>xvii</sup>	113.37 (6)
O3 <sup>viii</sup> —K1—O3 <sup>x</sup>	95.627 (13)	Na1 <sup>i</sup> —O1—K3 <sup>xvii</sup>	101.79 (5)
O3 <sup>ix</sup> —K1—O3 <sup>x</sup>	95.627 (13)	S1—O1—K4 <sup>xviii</sup>	87.35 (5)
O3 <sup>viii</sup> —K1—O3 <sup>i</sup>	95.627 (13)	Na1 <sup>i</sup> —O1—K4 <sup>xviii</sup>	97.05 (5)
O3 <sup>ix</sup> —K1—O3 <sup>i</sup>	95.627 (13)	K3 <sup>xvii</sup> —O1—K4 <sup>xviii</sup>	129.71 (5)
O3 <sup>x</sup> —K1—O3 <sup>i</sup>	143.50 (4)	S1—O2—K4 <sup>xix</sup>	130.46 (6)
O3 <sup>viii</sup> —K1—C13 <sup>ix</sup>	108.25 (2)	S1—O2—K3 <sup>xi</sup>	120.98 (6)
O3 <sup>ix</sup> —K1—C13 <sup>ix</sup>	108.25 (2)	K4 <sup>xix</sup> —O2—K3 <sup>xi</sup>	101.95 (3)
O3 <sup>x</sup> —K1—C13 <sup>ix</sup>	71.75 (2)	S1—O2—K4 <sup>xviii</sup>	100.28 (6)
O3 <sup>i</sup> —K1—C13 <sup>ix</sup>	71.75 (2)	K4 <sup>xix</sup> —O2—K4 <sup>xviii</sup>	95.61 (3)
O3 <sup>viii</sup> —K1—C13 <sup>i</sup>	71.75 (2)	K3 <sup>xi</sup> —O2—K4 <sup>xviii</sup>	99.20 (3)
O3 <sup>ix</sup> —K1—C13 <sup>i</sup>	71.75 (2)	S1—O3—K1 <sup>i</sup>	119.41 (6)
O3 <sup>x</sup> —K1—C13 <sup>i</sup>	108.25 (2)	S1—O3—K3 <sup>i</sup>	127.26 (6)
O3 <sup>i</sup> —K1—C13 <sup>i</sup>	108.25 (2)	K1 <sup>i</sup> —O3—K3 <sup>i</sup>	93.33 (3)
C13 <sup>ix</sup> —K1—C13 <sup>i</sup>	180.0	S1—O3—K4 <sup>xx</sup>	121.17 (6)
O6—K2—O6 <sup>viii</sup>	86.115 (12)	K1 <sup>i</sup> —O3—K4 <sup>xx</sup>	93.38 (3)
O6—K2—O6 <sup>xi</sup>	86.115 (12)	K3 <sup>i</sup> —O3—K4 <sup>xx</sup>	94.04 (3)
O6 <sup>viii</sup> —K2—O6 <sup>xi</sup>	149.82 (5)	O6—S2—O5	114.61 (7)
O6—K2—O6 <sup>xii</sup>	149.82 (5)	O6—S2—O4	114.50 (7)
O6 <sup>viii</sup> —K2—O6 <sup>xii</sup>	86.115 (12)	O5—S2—O4	113.86 (7)
O6 <sup>xi</sup> —K2—O6 <sup>xii</sup>	86.115 (12)	O6—S2—S2 <sup>xxi</sup>	105.01 (5)
O6—K2—C12	105.09 (2)	O5—S2—S2 <sup>xxi</sup>	103.10 (6)
O6 <sup>viii</sup> —K2—C12	105.09 (2)	O4—S2—S2 <sup>xxi</sup>	103.96 (5)



O6 <sup>xi</sup> —K2—C12	105.09 (2)	S2—O5—Na2 <sup>vii</sup>	127.70 (8)
O6 <sup>xii</sup> —K2—C12	105.09 (2)	S2—O5—K3 <sup>xxiii</sup>	111.41 (6)
O6—K2—C11	74.91 (2)	Na2 <sup>vii</sup> —O5—K3 <sup>xxiii</sup>	103.01 (4)
O6 <sup>viii</sup> —K2—C11	74.91 (2)	S2—O5—K4 <sup>xxii</sup>	89.49 (5)
O6 <sup>xi</sup> —K2—C11	74.91 (2)	Na2 <sup>vii</sup> —O5—K4 <sup>xxii</sup>	96.35 (4)
O6 <sup>xii</sup> —K2—C11	74.91 (2)	K3 <sup>xxiii</sup> —O5—K4 <sup>xxii</sup>	131.31 (5)
C12—K2—C11	180.0	S2—O6—K2	121.42 (6)
O4 <sup>viii</sup> —K3—O2 <sup>viii</sup>	155.78 (4)	S2—O6—K4 <sup>xii</sup>	130.44 (6)
O4 <sup>viii</sup> —K3—O4 <sup>xii</sup>	111.31 (5)	K2—O6—K4 <sup>xii</sup>	90.43 (3)
O2 <sup>viii</sup> —K3—O4 <sup>xii</sup>	83.34 (3)	S2—O6—K4 <sup>viii</sup>	119.60 (6)
O4 <sup>viii</sup> —K3—O3 <sup>i</sup>	74.78 (3)	K2—O6—K4 <sup>viii</sup>	89.00 (3)
O2 <sup>viii</sup> —K3—O3 <sup>i</sup>	96.76 (3)	K4 <sup>xii</sup> —O6—K4 <sup>viii</sup>	95.50 (3)
O4 <sup>xii</sup> —K3—O3 <sup>i</sup>	163.31 (3)	Na1 <sup>xxiv</sup> —C11—K2	180.0
O4 <sup>viii</sup> —K3—O1 <sup>iii</sup>	129.10 (4)	Na1 <sup>xxiv</sup> —C11—K4	96.394 (14)
O2 <sup>viii</sup> —K3—O1 <sup>iii</sup>	65.88 (3)	K2—C11—K4	83.606 (14)
O4 <sup>xii</sup> —K3—O1 <sup>iii</sup>	93.82 (3)	Na1 <sup>xxiv</sup> —C11—K4 <sup>xii</sup>	96.394 (14)
O3 <sup>i</sup> —K3—O1 <sup>iii</sup>	71.28 (3)	K2—C11—K4 <sup>xii</sup>	83.606 (14)
O4 <sup>viii</sup> —K3—O5 <sup>vi</sup>	75.96 (3)	K4—C11—K4 <sup>xii</sup>	167.21 (3)
O2 <sup>viii</sup> —K3—O5 <sup>vi</sup>	94.81 (3)	Na1 <sup>xxiv</sup> —C11—K4 <sup>viii</sup>	96.394 (14)
O4 <sup>xii</sup> —K3—O5 <sup>vi</sup>	64.12 (3)	K2—C11—K4 <sup>viii</sup>	83.606 (14)
O3 <sup>i</sup> —K3—O5 <sup>vi</sup>	132.27 (4)	K4—C11—K4 <sup>viii</sup>	89.290 (3)
O1 <sup>iii</sup> —K3—O5 <sup>vi</sup>	153.02 (3)	K4 <sup>xii</sup> —C11—K4 <sup>viii</sup>	89.289 (3)
O4 <sup>viii</sup> —K3—C13 <sup>ix</sup>	80.21 (2)	Na1 <sup>xxiv</sup> —C11—K4 <sup>xi</sup>	96.394 (14)
O2 <sup>viii</sup> —K3—C13 <sup>ix</sup>	75.58 (2)	K2—C11—K4 <sup>xi</sup>	83.606 (14)
O4 <sup>xii</sup> —K3—C13 <sup>ix</sup>	126.11 (2)	K4—C11—K4 <sup>xi</sup>	89.289 (3)
O3 <sup>i</sup> —K3—C13 <sup>ix</sup>	69.55 (2)	K4 <sup>xii</sup> —C11—K4 <sup>xi</sup>	89.289 (3)
O1 <sup>iii</sup> —K3—C13 <sup>ix</sup>	119.90 (3)	K4 <sup>viii</sup> —C11—K4 <sup>xi</sup>	167.21 (3)
O5 <sup>vi</sup> —K3—C13 <sup>ix</sup>	68.94 (3)	Na1—C12—K2	180.0
O4 <sup>viii</sup> —K3—C12	74.58 (2)	Na1—C12—K3	88.815 (12)
O2 <sup>viii</sup> —K3—C12	129.30 (2)	K2—C12—K3	91.185 (12)
O4 <sup>xii</sup> —K3—C12	73.07 (2)	Na1—C12—K3 <sup>viii</sup>	88.814 (12)
O3 <sup>i</sup> —K3—C12	94.52 (3)	K2—C12—K3 <sup>viii</sup>	91.186 (12)
O1 <sup>iii</sup> —K3—C12	71.59 (3)	K3—C12—K3 <sup>viii</sup>	89.976 (1)
O5 <sup>vi</sup> —K3—C12	112.82 (3)	Na1—C12—K3 <sup>xi</sup>	88.815 (12)
C13 <sup>ix</sup> —K3—C12	153.089 (9)	K2—C12—K3 <sup>xi</sup>	91.185 (12)
O2 <sup>xiii</sup> —K4—O6 <sup>xii</sup>	73.54 (3)	K3—C12—K3 <sup>xi</sup>	89.975 (1)
O2 <sup>xiii</sup> —K4—O6 <sup>xi</sup>	144.06 (3)	K3 <sup>viii</sup> —C12—K3 <sup>xi</sup>	177.63 (2)
O6 <sup>xii</sup> —K4—O6 <sup>xi</sup>	81.16 (4)	Na1—C12—K3 <sup>xii</sup>	88.814 (12)
O2 <sup>xiii</sup> —K4—O4 <sup>xiv</sup>	150.56 (4)	K2—C12—K3 <sup>xii</sup>	91.186 (12)
O6 <sup>xii</sup> —K4—O4 <sup>xiv</sup>	112.11 (3)	K3—C12—K3 <sup>xii</sup>	177.63 (2)
O6 <sup>xi</sup> —K4—O4 <sup>xiv</sup>	63.40 (3)	K3 <sup>viii</sup> —C12—K3 <sup>xii</sup>	89.975 (1)
O2 <sup>xiii</sup> —K4—O3 <sup>xv</sup>	94.02 (3)	K3 <sup>xi</sup> —C12—K3 <sup>xii</sup>	89.975 (1)
O6 <sup>xii</sup> —K4—O3 <sup>xv</sup>	156.61 (4)	Na2 <sup>vii</sup> —C13—K1 <sup>i</sup>	180.0
O6 <sup>xi</sup> —K4—O3 <sup>xv</sup>	117.73 (3)	Na2 <sup>vii</sup> —C13—K3 <sup>xi</sup>	93.559 (11)
O4 <sup>xiv</sup> —K4—O3 <sup>xv</sup>	69.49 (3)	K1 <sup>i</sup> —C13—K3 <sup>xi</sup>	86.441 (11)
O2 <sup>xiii</sup> —K4—O2 <sup>xvi</sup>	116.96 (4)	Na2 <sup>vii</sup> —C13—K3 <sup>xxv</sup>	93.559 (11)
O6 <sup>xii</sup> —K4—O2 <sup>xvi</sup>	140.54 (3)	K1 <sup>i</sup> —C13—K3 <sup>xxv</sup>	86.441 (11)
O6 <sup>xi</sup> —K4—O2 <sup>xvi</sup>	69.44 (3)	K3 <sup>xi</sup> —C13—K3 <sup>xxv</sup>	172.88 (2)

O4 <sup>xiv</sup> —K4—O2 <sup>xvi</sup>	77.97 (3)	Na2 <sup>vii</sup> —Cl3—K4 <sup>xxii</sup>	91.846 (11)
O3 <sup>xv</sup> —K4—O2 <sup>xvi</sup>	62.72 (3)	K1 <sup>i</sup> —Cl3—K4 <sup>xxii</sup>	88.154 (10)
O2 <sup>xiii</sup> —K4—Cl1	77.20 (2)	K3 <sup>xi</sup> —Cl3—K4 <sup>xxii</sup>	88.576 (7)
O6 <sup>xii</sup> —K4—Cl1	71.69 (2)	K3 <sup>xxv</sup> —Cl3—K4 <sup>xxii</sup>	91.195 (7)
O6 <sup>xi</sup> —K4—Cl1	70.78 (2)	Na2 <sup>vii</sup> —Cl3—K4 <sup>xix</sup>	91.846 (10)
O4 <sup>xiv</sup> —K4—Cl1	132.25 (2)	K1 <sup>i</sup> —Cl3—K4 <sup>xix</sup>	88.154 (10)
O3 <sup>xv</sup> —K4—Cl1	125.74 (3)	K3 <sup>xi</sup> —Cl3—K4 <sup>xix</sup>	91.195 (7)
O2 <sup>xvi</sup> —K4—Cl1	74.06 (2)	K3 <sup>xxv</sup> —Cl3—K4 <sup>xix</sup>	88.576 (7)
O2 <sup>xiii</sup> —K4—Cl3 <sup>xiv</sup>	75.23 (2)	K4 <sup>xxii</sup> —Cl3—K4 <sup>xix</sup>	176.31 (2)

Symmetry codes: (i)  $-x+1, -y+1, -z$ ; (ii)  $x-1/2, y-1/2, -z$ ; (iii)  $-y+1, x-1/2, -z$ ; (iv)  $y-1/2, -x+1, -z$ ; (v)  $x, y, z-1$ ; (vi)  $x+1/2, y-1/2, -z+1$ ; (vii)  $-x+1, -y+1, -z+1$ ; (viii)  $y, -x+1/2, z$ ; (ix)  $-y+3/2, x, z$ ; (x)  $x+1/2, y-1/2, -z$ ; (xi)  $-y+1/2, x, z$ ; (xii)  $-x+1/2, -y+1/2, z$ ; (xiii)  $-y+1, x-1/2, -z+1$ ; (xiv)  $y-1/2, -x, -z+1$ ; (xv)  $-x+1/2, -y+1/2, z+1$ ; (xvi)  $x-1/2, y-1/2, -z+1$ ; (xvii)  $y+1/2, -x+1, -z$ ; (xviii)  $x+1/2, y+1/2, -z+1$ ; (xix)  $y+1/2, -x+1, -z+1$ ; (xx)  $-x+1/2, -y+1/2, z-1$ ; (xxi)  $-x, -y+1, -z+1$ ; (xxii)  $-y, x+1/2, -z+1$ ; (xxiii)  $x-1/2, y+1/2, -z+1$ ; (xxiv)  $x, y, z+1$ ; (xxv)  $y, -x+3/2, z$ .