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Crystal structure of $K_6[Zn(CO_3)_4]$

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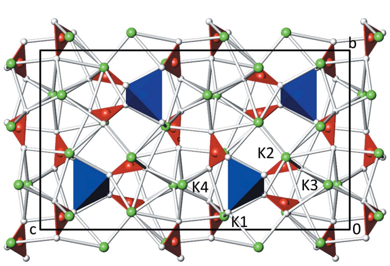
The crystal structure of $K_6[Zn(CO_3)_4]$, hexapotassium tetracarbonatozincate(II), comprises four unique potassium cations (two located on a general position, and two on the twofold rotation axis of the space group $C2/c$) and a $[Zn(CO_3)_4]^{6-}$ anion. The Zn^{II} atom of the latter is located on the twofold rotation axis and is surrounded in a slightly distorted tetrahedral manner by two pairs of monodentately binding carbonate groups, with Zn—O distances of 1.9554 (18) and 1.9839 (18) Å. Both carbonate groups exhibit a slight deviation from planarity, with the C atom being shifted by 0.008 (2) and 0.006 (3) Å, respectively, from the plane of the three O atoms. The coordination numbers of the potassium cations range from 6 to 8, using a threshold of 3.0 Å for K—O bonding interactions being significant. In the crystal structure, $[KO_x]$ polyhedra and $[Zn(CO_3)_4]^{6-}$ groups share O atoms to build up the framework structure.



1. Chemical context

Oxidotellurates(IV) exhibit a multifarious crystal chemistry (Christy *et al.*, 2016) that can be attributed to the different coordination numbers of Te^{IV} (usually between 3 and 5) in an oxidic environment and, particularly, to the stereoactive non-bonding $5s^2$ electron lone pair at the Te^{IV} atom (Galy *et al.*, 1975). The space requirement of the lone pair leads to unilateral coordination polyhedra $[Te^{IV}O_x]$ with rather low point-group symmetries. From a crystal-engineering point of view, $[Te^{IV}O_x]$ units are promising building blocks for the construction of new ferro-, pyro- or piezoelectric compounds or materials exhibiting non-linear optical behaviour like second-harmonic generation, as such compounds need to crystallize in non-centrosymmetric space groups with polar axes (Ok *et al.*, 2006).

In the quest to obtain new transition-metal oxidotellurates(IV) modified by addition of alkali cations, we developed syntheses under pseudo-hydrothermal conditions where water does not act as a typical solvent but rather as a mineralizer (Eder & Weil, 2022; Eder *et al.*, 2022, 2023). Characteristic for this kind of preparation method, only a few drops of water are added to the reaction mixture instead of the few millilitres typically used in a hydrothermal experiment. In an alternative route employed also for the present study, water is not added at all to the reaction mixture but originates from the initial decomposition of one of the educt(s) in the closed reaction container where it then acts as a mineralizing agent. Simultaneously, the employed oxidotellurate(VI) phase can be reduced under these conditions to an oxidotellurate(IV). In this sense, solid K_2CO_3, ZnO and H_6TeO_6 (as the source for water) were treated thermally under these conditions. However, the reaction did not result in an intended potassium

Table 1
Selected geometric parameters (Å, °).

Zn1—O4	1.9554 (18)	O2—C1	1.273 (3)
Zn1—O4^{i}	1.9554 (18)	O3—C1	1.278 (3)
Zn1—O1^{i}	1.9838 (18)	O4—C2	1.313 (3)
Zn1—O1	1.9839 (18)	O5—C2^{ii}	1.268 (3)
O1—C1	1.319 (3)	O6—C2	1.273 (3)
O4—Zn1—O4^{i}	113.95 (11)	O2—C1—O1	120.1 (2)
O4—Zn1—O1^{i}	99.62 (8)	O3—C1—O1	118.3 (2)
O4—Zn1—O1	114.01 (8)	O5^{ii}—C2—O6	123.1 (3)
O1^{i}—Zn1—O1	116.44 (10)	O5^{ii}—C2—O4	118.0 (2)
O2—C1—O3	121.7 (2)	O6—C2—O4	119.0 (2)

Symmetry codes: (i) $-x, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

zinc oxidotellurate(IV) phase. Instead, $K_6[Zn(CO_3)_4]$ was one of the obtained products, and its crystal structure is reported in the present communication.

2. Structural commentary

Of the 13 atoms (4 K, 1 Zn, 2 C, 6 O) in the asymmetric unit of $K_6[Zn(CO_3)_4]$, three are located on the twofold rotation axis (Zn1, K3, K4; Wyckoff position 4 *e*) of the space group *C*2/*c*. The remaining ten all are located on the general 8 *f* position. The most peculiar structural feature in the crystal structure is the tetracarbonatozincate(II) anion, $[Zn(CO_3)_4]^{6-}$, for which bond lengths and angles are given in Table 1. The Zn^{II} atom is surrounded in a slightly distorted tetrahedral manner by two pairs of monodentately binding carbonate groups (Fig. 1). The mean Zn—O distance of 1.976 Å conforms with the value of 1.952 (31) Å for Zn with a coordination number (CN) of 4 (Gagné & Hawthorne, 2020). The deviation from the ideal tetrahedral shape is small (Table 1), as indicated by the τ_4 index of 0.92 (τ_4 = 1 for an ideal tetrahedron; Yang *et al.*, 2007). In the carbonate groups, the mean C—O bond lengths of 1.290 (25) Å for C1 and 1.285 (25) Å for C2 are in very good agreement with the grand mean bond length of 1.284 (20) Å calculated from 389 individual carbonate groups (Gagné & Hawthorne, 2018). In the title compound, the longest C—O bond of ≃ 1.315 Å occurs for the O atoms that are bonded to the Zn^{II} atom. The angular distortions of the carbonate groups are minute (Table 1), with an angular sum of 360° in each case. However, both CO_3^{2-} groups in the $[Zn(CO_3)_4]^{6-}$ anion are aplanar, with the C atoms slightly shifted out of the plane of the three O atoms [C1 by −0.008 (2) Å from the plane defined by O1, O2, O3 and C2 by −0.006 (3) Å from O4, O5, O6]. Such a deviation from planarity is a frequently observed phenomenon for carbonate groups (Zemann, 1981; Winkler *et al.*, 2000).

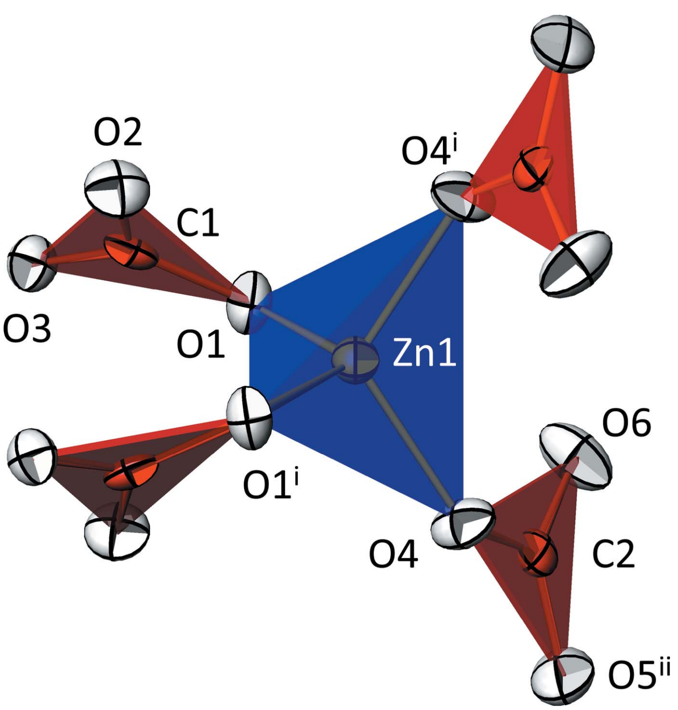


Figure 1
The tetrahedral $[Zn(CO_3)_4]^{6-}$ anion in the crystal structure of $K_6[Zn(CO_3)_4]$, with displacement ellipsoids drawn at the 74% probability level. [Symmetry codes: (i) $-x, y, -z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.]

The charge of the $[Zn(CO_3)_4]^{6-}$ anion is compensated by large potassium cations. Since coordination numbers of large cations are not always simple to derive because there is no clear boundary for longer bonds and the corresponding (weak) interactions between the central atom and the ligand atom (Gagné & Hawthorne, 2016), we defined a threshold of 3.0 Å for K—O interactions as being significant in $K_6[Zn(CO_3)_4]$. Based on this value, K1 and K2 have a CN of 7, K3 of 8 and K4 of 6, with distorted [KO$_x$] polyhedra in each case. The mean K—O bond lengths of 2.852 Å (K1), 2.763 Å (K2), 2.809 Å (K3) and 2.814 Å (K4) roughly correlate with literature values (Gagné & Hawthorne, 2016) of 2.828 (177) Å for a CN of 6, 2.861 (179) Å for a CN of 7, and 2.894 (172) Å for a CN of 8. The large standard deviations of the literature data likewise reflect the difficulties in defining coordination numbers for large cations.

Bond-valence sums (Brown, 2002) were calculated with the values provided by Brese & O'Keeffe (1991). Individual values (in valence units) are collated in the following list and

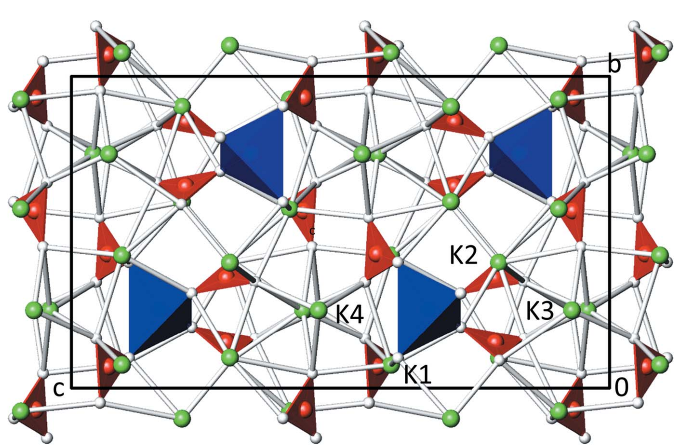


Figure 2
The crystal structure of $K_6[Zn(CO_3)_4]$ in a projection along [$\bar{1}$00]. Carbonate groups are shown as flattened red polyhedra and [ZnO$_4$] units as blue tetrahedra. All atoms are drawn as spheres of arbitrary radii (K green, O white, Zn blue, C red).

are in agreement with the expected values of 1 for K, 2 for Zn, 4 for C and 2 for O: K1: 1.02; K2: 1.31; K3: 1.32; K4: 0.96; Zn1: 1.95; C1: 3.84; C2: 3.99; O1 (CN = 4 with C, Zn, 2K): 1.94; O2 (CN = 5 with C, 4K): 1.92; O3 (CN = 6 with C, 5K): 2.18; O4 (CN = 4 with C, Zn, 2K): 2.00; O5 (CN = 5 with C, 4K): 1.92; O6 (CN = 5 with C, 4K): 1.92.

In the crystal structure of $K_6[Zn(CO_3)_4]$, $[KO_x]$ polyhedra and the isolated $[Zn(CO_3)_4]^{6-}$ anions share O atoms to build up a framework (Fig. 2).

3. Database survey

A search in the Inorganic Structure Database (ICSD, version April 2022; Zagorac *et al.*, 2019) for mixed alkali-metal/transition-metal carbonates revealed only eight anhydrous phases, *viz*. $Na_2Cu(CO_3)_2$ (Healy & White, 1972), $K_2Cu(CO_3)_2$ (Farrand *et al.*, 1980), $Na_3Y(CO_3)_3$ (Luo *et al.*, 2014), $Na_5Y(CO_3)_4$ (Awaleh *et al.*, 2003), $KY(CO_3)_2$ (Cao *et al.*, 2018), $Na_2Cd(CO_3)_2$ (Kim *et al.*, 2018), $K_2Cd(CO_3)_2$ (Kim *et al.*, 2021), and $KAgCO_3$ (Hans *et al.*, 2015). This makes $K_6[Zn(CO_3)_4]$ the phase with the highest quantity of an alkali metal. Except for the two copper(II) compounds where Cu^{II} shows a square-planar coordination by carbonate O atoms, the coordination numbers of all other transition metals are higher than 4.

However, numerous hydrous mixed alkali-metal/transition-metal carbonates are known. Limited to mixed alkali-metal zinc carbonates, these are: $LiZn(CO_3)(OH)$ (Liu *et al.*, 2021), $NaZn(CO_3)(OH)$ (Peng *et al.*, 2020), $Na_2Zn_3(CO_3)_4\cdot 3H_2O$ (Gier *et al.*, 1996), $NaK_2\{Zn_2[H(CO_3)_2](CO_3)_2(H_2O)_2$ and $NaRb_2\{Zn_2[H(CO_3)_2](CO_3)_2(H_2O)_2$ (Zheng & Adam, 1995).

In the crystal structure of $LiZn(CO_3)(OH)$, the Zn^{II} atom is tetrahedrally coordinated by two O atoms of monodentate carbonate groups and two bridging OH groups, leading to ${}^{1}_{\infty}[ZnO_{2/1}(OH)_{2/2}]$ chains extending parallel to [100] that are bridged by the carbonate groups into layers. In $NaZn(CO_3)(OH)$, the Zn^{II} atom is likewise tetrahedrally coordinated by two O atoms of monodentate carbonate groups and two OH groups, leading to isolated $[ZnO_2(OH)_2]$ tetrahedra. In the crystal structure of $Na_2Zn_3(CO_3)_4\cdot 3H_2O$, the Zn^{II} atom is coordinated tetrahedrally by four oxygen atoms belonging to four carbonate ions. Each carbonate group binds to three different zinc atoms forming an open framework structure. Finally, in $NaK_2\{Zn_2[H(CO_3)_2](CO_3)_2(H_2O)_2$ and isotypic $NaRb_2\{Zn_2[H(CO_3)_2](CO_3)_2(H_2O)_2$, the Zn^{II} atom is coordinated by five oxygen atoms belonging to four carbonate groups and one water molecule. Very similarly, in $Na_3Zn_2(CO_3)_3F$ (Tang *et al.*, 2018) the same coordination number results by coordination from four carbonate groups and a fluoride anion.

4. Synthesis and crystallization

All employed educts were obtained from commercial sources and were chemically pure. Solid ZnO, H_6TeO_6 and K_2CO_3 were thoroughly mixed in the molar ratio 2:3:10 (original sample weights 0.0584 g, 0.2486 g, 0.4498 g, respectively) and locked in a Teflon container with an inner volume of about 3 ml. The container was sealed and placed in a steel autoclave that was heated for one week at 483 K. The obtained solid product was colourless, comprising the title compound in the form of a few colourless crystals with a plate-like form. Powder X-ray diffraction (PXRD) revealed $K_6[Zn(CO_3)_4]$, $K_2CO_3\cdot 1.5H_2O$ (Skakle *et al.*, 2001), $KTeO_3OH$ (Lindqvist, 1972) and the starting material ZnO as product phases with approximate contingents (in mass percentages) of 45%, 40%, 10% and <5%, respectively, together with some unassigned reflections of low intensities.

$K_6[Zn(CO_3)_4]$ could also be synthesized by slow evaporation of a solution containing $Zn(NO_3)_2\cdot 6H_2O$ and K_2CO_3 in a molar ratio of 1:5, resulting in an increased yield of the title compound (70%), together with $K_2CO_3\cdot 1.5H_2O$ (25%) and ZnO (<5%) as by-products, as determined by phase analysis on basis of PXRD data.

Table 2
Experimental details.

Crystal data	
Chemical formula	$K_6[Zn(CO_3)_4]$
M_r	540.01
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	296
a, *b*, *c* (Å)	7.1850 (6), 18.1117 (14), 10.5206 (8)
β (°)	93.579 (2)
V (Å^3)	1366.40 (19)
Z	4
Radiation type	Mo *K*α
μ (mm^{-1})	3.69
Crystal size (mm)	0.08 × 0.04 × 0.02
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.665, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8980, 2592, 1712
R_{int}	0.056
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.785
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.040, 0.072, 0.98
No. of reflections	2592
No. of parameters	106
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.02, −0.63

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *ATOMS* (Dowty, 2006), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Structure data were standardized with *STRUCTURE-TIDY* (Gelato & Parthé, 1987).

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Crystal structure of $K_6[Zn(CO_3)_4]$

Felix Eder and Matthias Weil

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

Hexapotassium tetracarbonatozincate(II)

Crystal data

$K_6[Zn(CO_3)_4]$	$F(000) = 1056$
$M_r = 540.01$	$D_x = 2.625$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 7.1850$ (6) Å	Cell parameters from 1545 reflections
$b = 18.1117$ (14) Å	$\theta = 4.5–29.4°$
$c = 10.5206$ (8) Å	$\mu = 3.69$ mm^{-1}
$\beta = 93.579$ (2)°	$T = 296$ K
$V = 1366.40$ (19) Å^3	Block, colourless
$Z = 4$	0.08 × 0.04 × 0.02 mm

Data collection

Bruker APEXII CCD diffractometer	2592 independent reflections
ω– and φ–scans	1712 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Krause *et al.*, 2015)	$R_{int} = 0.056$
$T_{min} = 0.665$, $T_{max} = 0.747$	$\theta_{max} = 33.9°$, $\theta_{min} = 3.0°$
8980 measured reflections	$h = -11 \rightarrow 11$
	$k = -26 \rightarrow 27$
	$l = -15 \rightarrow 16$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.072$	$\Delta\rho_{max} = 1.02$ e Å^{-3}
$S = 0.98$	$\Delta\rho_{min} = -0.63$ e Å^{-3}
2592 reflections	
106 parameters	

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Zn1	0.000000	0.33426 (2)	0.250000	0.01451 (11)
K1	0.34220 (9)	0.40604 (3)	0.07452 (6)	0.02200 (14)
K2	0.38485 (8)	0.20542 (3)	0.40224 (6)	0.02155 (14)
K3	0.000000	0.06967 (4)	0.250000	0.01697 (17)
K4	0.000000	0.54036 (5)	0.250000	0.0235 (2)
O1	0.2160 (3)	0.27658 (10)	0.19578 (18)	0.0184 (4)
O2	0.0052 (3)	0.20449 (10)	0.08928 (18)	0.0216 (4)
O3	0.2802 (2)	0.15837 (9)	0.15907 (16)	0.0169 (4)
O4	0.0538 (3)	0.39310 (10)	0.40374 (17)	0.0206 (4)
O5	0.2533 (3)	0.05284 (11)	0.45294 (18)	0.0264 (5)
O6	0.3006 (3)	0.45433 (11)	0.34053 (19)	0.0271 (5)
C1	0.1656 (4)	0.21218 (14)	0.1462 (2)	0.0146 (5)
C2	0.2048 (4)	0.43226 (13)	0.4310 (2)	0.0155 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0148 (2)	0.0142 (2)	0.0144 (2)	0.000	−0.00042 (17)	0.000
K1	0.0222 (3)	0.0204 (3)	0.0233 (3)	−0.0016 (2)	0.0010 (3)	−0.0040 (2)
K2	0.0210 (3)	0.0265 (3)	0.0168 (3)	0.0032 (3)	−0.0013 (2)	−0.0030 (2)
K3	0.0162 (4)	0.0160 (4)	0.0188 (4)	0.000	0.0014 (3)	0.000
K4	0.0177 (4)	0.0182 (4)	0.0339 (5)	0.000	−0.0038 (4)	0.000
O1	0.0173 (10)	0.0130 (8)	0.0250 (10)	−0.0008 (8)	0.0026 (8)	−0.0020 (8)
O2	0.0163 (9)	0.0263 (11)	0.0217 (10)	0.0018 (8)	−0.0035 (8)	0.0007 (8)
O3	0.0146 (9)	0.0161 (9)	0.0200 (10)	0.0034 (7)	0.0012 (8)	−0.0006 (7)
O4	0.0189 (10)	0.0259 (10)	0.0169 (10)	−0.0088 (8)	0.0005 (8)	−0.0049 (8)
O5	0.0317 (12)	0.0246 (10)	0.0213 (10)	−0.0024 (9)	−0.0100 (9)	−0.0034 (9)
O6	0.0193 (10)	0.0332 (12)	0.0290 (12)	−0.0050 (9)	0.0018 (9)	0.0138 (9)
C1	0.0152 (12)	0.0191 (13)	0.0097 (12)	0.0012 (10)	0.0022 (10)	0.0048 (10)
C2	0.0185 (13)	0.0128 (12)	0.0149 (13)	0.0029 (10)	−0.0028 (11)	0.0026 (10)

Geometric parameters (Å, º)

Zn1—O4	1.9554 (18)	K3—O5	2.7344 (19)
Zn1—O4^{i}	1.9554 (18)	K3—O6^{ix}	2.738 (2)
Zn1—O1^{i}	1.9838 (18)	K3—O6^{x}	2.738 (2)
Zn1—O1	1.9839 (18)	K3—O3	2.7910 (18)
K1—O5^{ii}	2.756 (2)	K3—O3^{i}	2.7910 (18)
K1—O6^{iii}	2.804 (2)	K3—O2^{i}	2.972 (2)

K1—O3^{iv}	2.8113 (18)	K3—O2	2.972 (2)
K1—O1	2.8448 (19)	K3—C1^{i}	3.071 (3)
K1—O4^{i}	2.879 (2)	K3—C1	3.071 (3)
K1—O2^{iv}	2.901 (2)	K3—K4^{ix}	3.6315 (3)
K1—O6	2.965 (2)	K3—K4^{xi}	3.6315 (3)
K1—C1^{iv}	3.156 (3)	K4—O6^{i}	2.782 (2)
K1—C2^{iii}	3.293 (3)	K4—O6	2.783 (2)
K1—O5^{v}	3.374 (2)	K4—O3^{ii}	2.7908 (18)
K1—C2^{vi}	3.412 (3)	K4—O3^{xii}	2.7908 (18)
K2—O2^{vii}	2.6590 (19)	K4—O5^{xii}	2.868 (2)
K2—O3^{iii}	2.6697 (19)	K4—O5^{ii}	2.868 (2)
K2—O4^{viii}	2.726 (2)	K4—C2	3.046 (2)
K2—O1	2.7426 (19)	K4—C2^{i}	3.046 (2)
K2—O3	2.7561 (18)	K4—O4^{i}	3.131 (2)
K2—O2^{i}	2.810 (2)	K4—O4	3.131 (2)
K2—O5	2.980 (2)	O1—C1	1.319 (3)
K2—C1	3.037 (3)	O2—C1	1.273 (3)
K2—C2^{viii}	3.139 (3)	O3—C1	1.278 (3)
K2—C1^{iii}	3.303 (3)	O4—C2	1.313 (3)
K2—K2^{viii}	3.3304 (12)	O5—C2^{viii}	1.268 (3)
K2—O1^{iii}	3.3644 (19)	O6—C2	1.273 (3)
K3—O5^{i}	2.7344 (19)		

O4—Zn1—O4^{i}	113.95 (11)	O6^{i}—K4—O5^{xii}	78.24 (6)
O4—Zn1—O1^{i}	99.62 (8)	O6—K4—O5^{xii}	106.98 (6)
O4^{i}—Zn1—O1^{i}	114.01 (8)	O3^{ii}—K4—O5^{xii}	92.71 (5)
O4—Zn1—O1	114.01 (8)	O3^{xii}—K4—O5^{xii}	80.33 (5)
O4^{i}—Zn1—O1	99.62 (8)	O6^{i}—K4—O5^{ii}	106.98 (6)
O1^{i}—Zn1—O1	116.44 (10)	O6—K4—O5^{ii}	78.24 (6)
O5^{ii}—K1—O6^{iii}	87.09 (6)	O3^{ii}—K4—O5^{ii}	80.33 (5)
O5^{ii}—K1—O3^{iv}	104.27 (6)	O3^{xii}—K4—O5^{ii}	92.71 (5)
O6^{iii}—K1—O3^{iv}	129.66 (6)	O5^{xii}—K4—O5^{ii}	170.96 (8)
O5^{ii}—K1—O1	139.27 (6)	O6^{i}—K4—O4^{i}	43.77 (5)
O6^{iii}—K1—O1	115.16 (6)	O6—K4—O4^{i}	76.59 (6)
O3^{iv}—K1—O1	87.64 (5)	O3^{ii}—K4—O4^{i}	151.47 (5)
O5^{ii}—K1—O4^{i}	81.15 (6)	O3^{xii}—K4—O4^{i}	115.23 (5)
O6^{iii}—K1—O4^{i}	152.83 (6)	O5^{xii}—K4—O4^{i}	112.93 (6)
O3^{iv}—K1—O4^{i}	77.22 (5)	O5^{ii}—K4—O4^{i}	75.21 (5)
O1—K1—O4^{i}	63.44 (5)	C2—K4—O4^{i}	79.32 (6)
O5^{ii}—K1—O2^{iv}	134.76 (6)	C2^{i}—K4—O4^{i}	24.49 (6)
O6^{iii}—K1—O2^{iv}	91.85 (6)	O6^{i}—K4—O4	76.59 (6)
O3^{iv}—K1—O2^{iv}	45.86 (5)	O6—K4—O4	43.77 (5)
O1—K1—O2^{iv}	80.82 (5)	O3^{ii}—K4—O4	115.23 (5)
O4^{i}—K1—O2^{iv}	113.78 (6)	O3^{xii}—K4—O4	151.47 (5)
O5^{ii}—K1—O6	77.01 (6)	O5^{xii}—K4—O4	75.21 (5)
O6^{iii}—K1—O6	75.60 (6)	O5^{ii}—K4—O4	112.93 (6)
O3^{iv}—K1—O6	154.55 (6)	C2—K4—O4	24.49 (6)
O1—K1—O6	76.47 (5)	C2^{i}—K4—O4	79.32 (6)

O4^{i}—K1—O6	77.91 (6)	O4^{i}—K4—O4	63.16 (7)
O2^{iv}—K1—O6	145.94 (6)	C1—O1—Zn1	112.29 (16)
O5^{ii}—K1—O5^{v}	88.01 (6)	C1—O1—K2	89.70 (14)
O6^{iii}—K1—O5^{v}	41.12 (5)	Zn1—O1—K2	109.58 (8)
O3^{iv}—K1—O5^{v}	89.64 (5)	C1—O1—K1	129.69 (16)
O1—K1—O5^{v}	131.53 (5)	Zn1—O1—K1	88.39 (6)
O4^{i}—K1—O5^{v}	160.24 (5)	K2—O1—K1	127.22 (7)
O2^{iv}—K1—O5^{v}	63.57 (5)	C1—O1—K2^{iii}	76.00 (13)
O6—K1—O5^{v}	115.78 (5)	Zn1—O1—K2^{iii}	170.74 (8)
C1^{iv}—K1—O5^{v}	81.18 (6)	K2—O1—K2^{iii}	73.70 (5)
C2^{iii}—K1—O5^{v}	21.89 (5)	K1—O1—K2^{iii}	82.91 (5)
O2^{vii}—K2—O3^{iii}	96.79 (6)	C1—O2—K2^{xiii}	121.60 (16)
O2^{vii}—K2—O4^{viii}	79.50 (6)	C1—O2—K2^{i}	149.34 (17)
O3^{iii}—K2—O4^{viii}	82.30 (6)	K2^{xiii}—O2—K2^{i}	74.98 (5)
O2^{vii}—K2—O1	113.90 (6)	C1—O2—K1^{iv}	89.44 (15)
O3^{iii}—K2—O1	108.64 (6)	K2^{xiii}—O2—K1^{iv}	95.82 (6)
O4^{viii}—K2—O1	160.62 (6)	K2^{i}—O2—K1^{iv}	115.96 (7)
O2^{vii}—K2—O3	159.06 (6)	C1—O2—K3	82.28 (14)
O3^{iii}—K2—O3	82.81 (6)	K2^{xiii}—O2—K3	155.54 (8)
O4^{viii}—K2—O3	120.97 (6)	K2^{i}—O2—K3	86.49 (5)
O1—K2—O3	47.83 (5)	K1^{iv}—O2—K3	77.86 (5)
O2^{vii}—K2—O2^{i}	105.02 (5)	C1—O3—K2^{iii}	108.39 (15)
O3^{iii}—K2—O2^{i}	157.18 (6)	C1—O3—K2	89.96 (14)
O4^{viii}—K2—O2^{i}	95.00 (6)	K2^{iii}—O3—K2	85.86 (5)
O1—K2—O2^{i}	68.60 (5)	C1—O3—K4^{xi}	165.41 (16)
O3—K2—O2^{i}	79.21 (6)	K2^{iii}—O3—K4^{xi}	80.09 (5)
O2^{vii}—K2—O5	121.93 (6)	K2—O3—K4^{xi}	78.63 (5)
O3^{iii}—K2—O5	92.76 (6)	C1—O3—K3	90.09 (15)
O4^{viii}—K2—O5	45.34 (5)	K2^{iii}—O3—K3	161.25 (7)
O1—K2—O5	116.61 (6)	K2—O3—K3	91.18 (5)
O3—K2—O5	78.94 (5)	K4^{xi}—O3—K3	81.17 (5)
O2^{i}—K2—O5	70.15 (6)	C1—O3—K1^{iv}	93.41 (14)
O2^{vii}—K2—O1^{iii}	75.38 (5)	K2^{iii}—O3—K1^{iv}	99.14 (6)
O3^{iii}—K2—O1^{iii}	41.38 (5)	K2—O3—K1^{iv}	172.75 (7)
O4^{viii}—K2—O1^{iii}	112.29 (5)	K4^{xi}—O3—K1^{iv}	96.97 (5)
O1—K2—O1^{iii}	85.45 (6)	K3—O3—K1^{iv}	82.40 (5)
O3—K2—O1^{iii}	91.28 (5)	C2—O4—Zn1	126.39 (17)
O2^{i}—K2—O1^{iii}	152.02 (5)	C2—O4—K2^{viii}	95.59 (14)
O5—K2—O1^{iii}	134.13 (5)	Zn1—O4—K2^{viii}	106.08 (8)
C1—K2—O1^{iii}	96.75 (6)	C2—O4—K1^{i}	138.26 (16)
C2^{viii}—K2—O1^{iii}	133.18 (6)	Zn1—O4—K1^{i}	87.97 (7)
C1^{iii}—K2—O1^{iii}	22.80 (5)	K2^{viii}—O4—K1^{i}	96.21 (6)
K2^{viii}—K2—O1^{iii}	122.93 (4)	C2—O4—K4	74.12 (13)
O5^{i}—K3—O5	167.20 (9)	Zn1—O4—K4	91.45 (7)
O5^{i}—K3—O6^{ix}	81.34 (6)	K2^{viii}—O4—K4	162.44 (7)
O5—K3—O6^{ix}	88.88 (6)	K1^{i}—O4—K4	83.15 (5)
O5^{i}—K3—O6^{x}	88.88 (6)	C2^{viii}—O5—K3	146.56 (17)
O5—K3—O6^{x}	81.33 (6)	C2^{viii}—O5—K1^{x}	110.41 (16)

O6^{ix}—K3—O6^{x}	80.53 (9)	K3—O5—K1^{x}	82.91 (6)
O5^{i}—K3—O3	104.81 (6)	C2^{viii}—O5—K4^{xi}	127.79 (17)
O5—K3—O3	82.69 (6)	K3—O5—K4^{xi}	80.78 (5)
O6^{ix}—K3—O3	164.34 (6)	K1^{x}—O5—K4^{xi}	90.42 (6)
O6^{x}—K3—O3	85.15 (6)	C2^{viii}—O5—K2	85.18 (15)
O5^{i}—K3—O3^{i}	82.69 (6)	K3—O5—K2	87.70 (6)
O5—K3—O3^{i}	104.81 (6)	K1^{x}—O5—K2	162.84 (8)
O6^{ix}—K3—O3^{i}	85.16 (6)	K4^{xi}—O5—K2	73.86 (5)
O6^{x}—K3—O3^{i}	164.34 (6)	C2^{viii}—O5—K1^{xiv}	75.47 (15)
O3—K3—O3^{i}	109.72 (7)	K3—O5—K1^{xiv}	73.49 (5)
O5^{i}—K3—O2^{i}	120.30 (6)	K1^{x}—O5—K1^{xiv}	91.99 (6)
O5—K3—O2^{i}	71.26 (6)	K4^{xi}—O5—K1^{xiv}	153.64 (7)
O6^{ix}—K3—O2^{i}	113.80 (6)	K2—O5—K1^{xiv}	99.10 (6)
O6^{x}—K3—O2^{i}	148.26 (5)	C2—O6—K3^{xv}	144.96 (18)
O3—K3—O2^{i}	75.94 (5)	C2—O6—K4	89.28 (15)
O3^{i}—K3—O2^{i}	45.33 (5)	K3^{xv}—O6—K4	82.27 (5)
O5^{i}—K3—O2	71.26 (6)	C2—O6—K1^{iii}	100.98 (15)
O5—K3—O2	120.30 (6)	K3^{xv}—O6—K1^{iii}	81.98 (5)
O6^{ix}—K3—O2	148.26 (5)	K4—O6—K1^{iii}	163.55 (8)
O6^{x}—K3—O2	113.80 (6)	C2—O6—K1	134.75 (17)
O3—K3—O2	45.34 (5)	K3^{xv}—O6—K1	79.10 (5)
O3^{i}—K3—O2	75.94 (5)	K4—O6—K1	87.93 (6)
O2^{i}—K3—O2	69.49 (8)	K1^{iii}—O6—K1	93.70 (6)
O6^{i}—K4—O6	111.90 (9)	O2—C1—O3	121.7 (2)
O6^{i}—K4—O3^{ii}	163.07 (6)	O2—C1—O1	120.1 (2)
O6—K4—O3^{ii}	84.32 (6)	O3—C1—O1	118.3 (2)
O6^{i}—K4—O3^{xii}	84.32 (6)	O5^{viii}—C2—O6	123.1 (3)
O6—K4—O3^{xii}	163.07 (6)	O5^{viii}—C2—O4	118.0 (2)
O3^{ii}—K4—O3^{xii}	80.03 (8)	O6—C2—O4	119.0 (2)

Symmetry codes: (i) $-x, y, -z+1/2$; (ii) $-x+1/2, y+1/2, -z+1/2$; (iii) $-x+1, y, -z+1/2$; (iv) $-x+1/2, -y+1/2, -z$; (v) $x+1/2, -y+1/2, z-1/2$; (vi) $x, -y+1, z-1/2$; (vii) $x+1/2, -y+1/2, z+1/2$; (viii) $-x+1/2, -y+1/2, -z+1$; (ix) $x-1/2, y-1/2, z$; (x) $-x+1/2, y-1/2, -z+1/2$; (xi) $x+1/2, y-1/2, z$; (xii) $x-1/2, y+1/2, z$; (xiii) $x-1/2, -y+1/2, z-1/2$; (xiv) $x-1/2, -y+1/2, z+1/2$; (xv) $x+1/2, y+1/2, z$.