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# Crystal structure of dipotassium *N*-carbodithioato-L-prolinate trihydrate

Phil Liebing\*

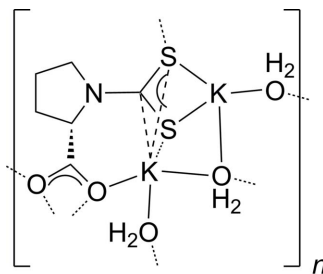
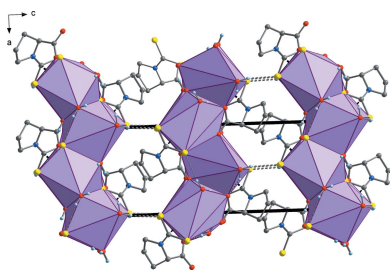
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The molecular and crystal structure of the L-proline-derived dithiocarbamate-carboxylate compound poly[tri- $\mu$ -aqua-( $\mu$ -2-carboxylatopyrrolidine-1-carbodithioato)dipotassium],  $[\text{K}_2(\text{C}_6\text{H}_7\text{NO}_2\text{S}_2)(\text{H}_2\text{O})_3]_n$  or  $\text{K}_2(\text{SSC-NC}_4\text{H}_7\text{-COO})\cdot 3\text{H}_2\text{O}$ , has been determined. The dithiocarbamate moiety displays a unique coordination mode, comprising a 'side-on'  $\pi$ -coordinated  $\text{K}^+$  cation besides a commonly  $\sigma$ -chelated  $\text{K}^+$  cation. By bridging coordination of the CSS group, COO group and water molecules, the  $\text{K}^+$  cations are linked into a two-dimensional coordination polymer extending parallel to the *ab* plane. These layers are again interconnected by  $\text{O}-\text{H}\cdots\text{S}$  hydrogen bonds.

## 1. Chemical context

Natural amino acids react readily with carbon disulfide in an alkaline environment to give dithiocarbamate-functionalized carboxylates. Since the first report on a series of barium salts in the 1950s (Zahradnik, 1956), numerous transition metal complexes have been explored. More recently, various late transition metal complexes of this family have been investigated due to their biological activity (*e.g.* Giovagnini *et al.*, 2005; Cachapa *et al.*, 2006; Nagy *et al.*, 2012). In most cases, the dithiocarbamate moiety acts as a classical small-bite chelate ligand, while the carboxylate group (often esterified) does not contribute to metal coordination. The structural chemistry of main group derivatives of dithiocarbamate-derived amino acids is much less explored, even though alkali metal and alkaline earth metal salts are frequently used as precursors for other metal complexes. A key intermediate in our ongoing research on coordination polymers with dithiocarbamate-carboxylates is the L-proline-derived potassium salt  $\text{K}_2(\text{SSC-NC}_4\text{H}_7\text{-COO})$ . This compound crystallizes from aqueous solution as a trihydrate, which has been structurally characterized in the course of this work.



## 2. Structural commentary

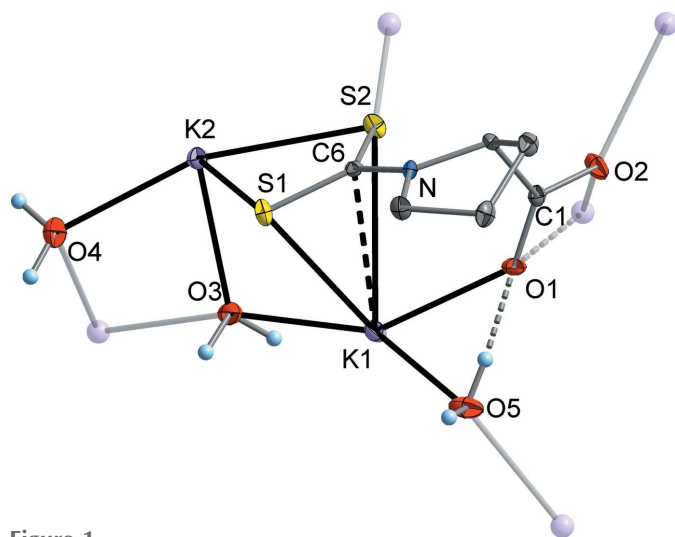
The title compound,  $\text{K}_2(\text{SSC-NC}_4\text{H}_7\text{-COO})\cdot 3\text{H}_2\text{O}$ , crystallized as colourless plates in the orthorhombic space group

**Table 1**  
 Hydrogen-bond geometry (Å, °).

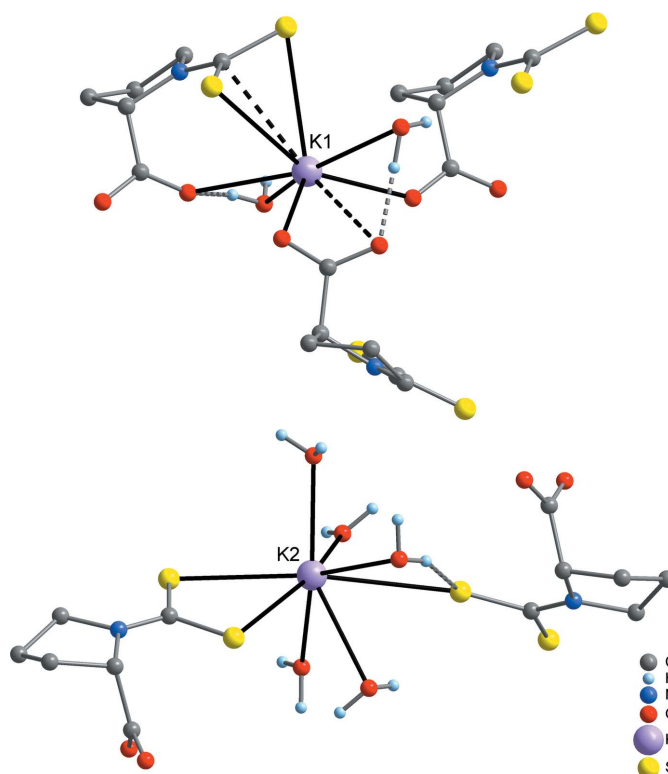
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O3-H9\cdots O1^i$	0.83 (2)	1.93 (2)	2.752 (3)	170 (4)
$O3-H8\cdots S2^{ii}$	0.81 (2)	2.57 (2)	3.3123 (19)	153 (3)
$O4-H11\cdots O2^{iii}$	0.80 (2)	2.22 (2)	3.000 (3)	166 (4)
$O5-H13\cdots O1$	0.81 (2)	1.99 (3)	2.724 (3)	150 (3)
$O5-H12\cdots S1^{iv}$	0.81 (2)	2.55 (2)	3.341 (2)	163 (3)

Symmetry codes: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 2$ ; (ii)  $x + 1, y, z$ ; (iii)  $x + 1, y + 1, z$ ; (iv)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

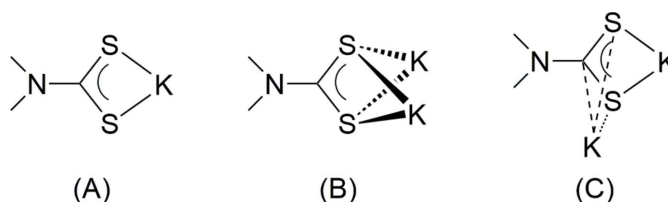
$P2_12_12_1$ , with one formula moiety in the asymmetric unit (Fig. 1). One K atom (K2) is bonded in a typical chelating fashion by the CSS group, while K1 is coordinated 'side-on' to the CSS group, certainly under participation of the delocalized  $\pi$  electrons. This rather uncommon coordination mode might be supported by additional coordination of a carboxylate O atom (O1) to K1. K1 adopts a low-symmetric seven-coordination by four carboxylate O atoms, two  $H_2O$  molecules and the  $\pi$ -coordinating CSS group. K2 is eight-coordinated by three S atoms and five  $H_2O$  molecules (Fig. 2). Consequently, the full coordination mode of the carboxylate group is  $\mu_3-\kappa^4O,O':O:O'$ , and the dithiocarbamate group adopts a  $\mu_3-\kappa^6S,S',C:S,S':S$  coordination. One  $H_2O$  molecule displays a  $\mu_3$ -coordination (O3) and the remaining two  $H_2O$  molecules are coordinating in a  $\mu$ -bridging mode (O4 and O5). The K–S distances at the  $\sigma$ -chelated  $K^+$  cation (K2) are 3.2176 (8) and 3.2650 (9) Å, while the K–S separations at the  $\pi$ -coordinated  $K^+$  cation (K1) are significantly longer at 3.2956 (9) and 3.4463 (8) Å. The coordination mode of the dithiocarbamate group in the title compound [see (C) in Fig. 3] is unique, to our knowledge. The most frequently observed coordination pattern in dithiocarbamates of the heavier alkali metals (K, Rb and Cs) is a symmetric double-chelating mode, leading to a puckered  $S_2M_2$  ring (e.g. Howie *et al.*, 2008; Reyes-Martínez



**Figure 1**  
 The asymmetric unit of the title compound. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level and H atoms attached to C atoms have been omitted for clarity. Adjacent symmetry-related  $K^+$  cations are illustrated as semi-transparent spheres.



**Figure 2**  
 Illustration of the coordination environment of the two  $K^+$  cations.

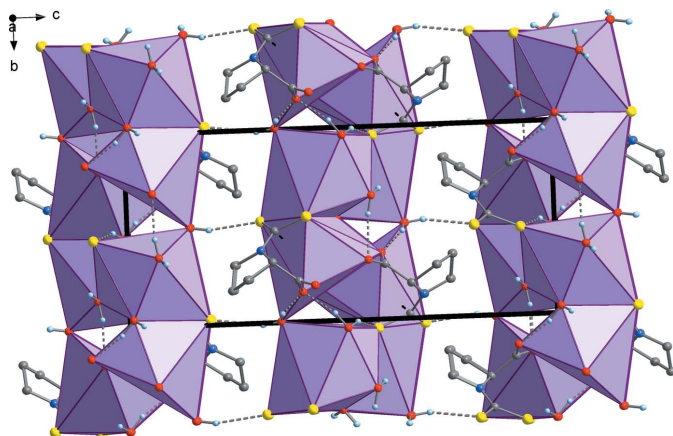


**Figure 3**  
 The different coordination modes of the dithiocarbamate group in potassium complexes: single-chelating (A), symmetric double-chelating (B) and single-chelating combined with  $\pi$ -coordination (this work; C).

*et al.*, 2009; Mafud, 2012; see (B) in Fig. 3]. Nonetheless, the values of the K–S separations in the title compound cover the same range as observed in the reference compounds. A simple chelating coordination with significantly shorter K–S contacts is realized when the  $K^+$  cation is coordinatively highly saturated, as has been observed in a crown ether complex [Arman *et al.*, 2013; see (A) in Fig. 3]. In the title compound, three of the four K–O(carboxylate) contacts are in a range 2.676 (2)–2.802 (2) Å, which is consistent with the values observed in other potassium carboxylates (e.g. Ilcyszyn *et al.*, 2009; Liebing *et al.*, 2016). However, one contact (K1'–O1) is strongly elongated to 3.358 (2) Å. The K–O( $H_2O$ ) bond lengths cover a range of 2.723 (2)–3.065 (3) Å.

### 3. Supramolecular features

As a result of the bridging coordination of the carboxylate group, the dithiocarbamate group and the water molecules, a two-dimensional polymeric structure parallel to the  $ab$  plane is



**Figure 4**  
Supramolecular crystal structure comprising polymeric layers extending parallel to (001), viewed in a projection on (100). The bold black lines mark the unit-cell dimensions.

built (Figs. 4 and 5). This arrangement is likely supported by  $O3-H \cdots O1^i$ ,  $O3-H \cdots S2^{ii}$ ,  $O4-H \cdots O2^{iii}$  and  $O5-H \cdots O1$  hydrogen bonds within the layer (Table 1). The layer surfaces are defined by the hydrophobic hydrocarbon backbones, but additionally the two-dimensional arrays are apparently interconnected by  $O5-H \cdots S1^{iv}$  hydrogen bonds.

#### 4. Database survey

For other potassium dithiocarbamates, see *e.g.* Cambridge Structural Database (CSD; Groom *et al.*, 2016) refcode AGEHIF (Arman *et al.*, 2013), KOLLIH (Howie *et al.*, 2008), LEHRUN (Mafud, 2012).

For other potassium carboxylates, see *e.g.* CONWOS (Ilczyszyn *et al.*, 2009), and BIFMIN01 and BIFMUZ01 (Liebing *et al.*, 2016).

#### 5. Synthesis and crystallization

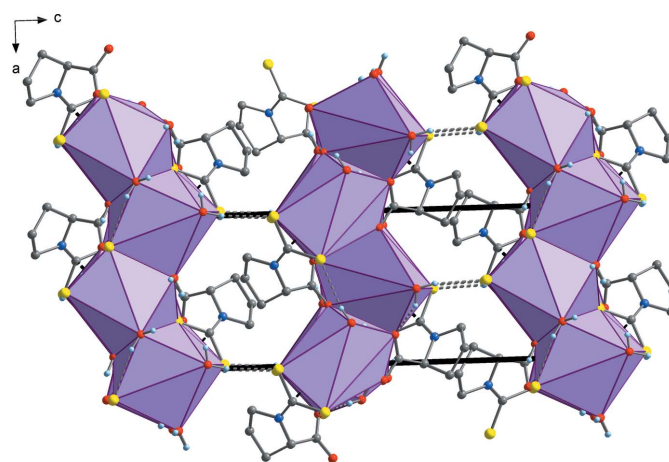
A slight excess of carbon disulfide (approximately 4 ml, 0.06 mol) was added to a solution of L-proline (5.76 g, 0.05 mol) and potassium hydroxide (5.61 g, 0.10 mol) in 30 ml water and the resulting solution was stirred vigorously overnight. The yellow solution obtained was filtered and reduced to dryness *in vacuo*. The crystalline residue was washed with several portions of tetrahydrofuran and diethyl ether, and dried *in vacuo*, providing analytically pure  $K_2(SSC-NC_4H_7-COO) \cdot 3H_2O$  in almost quantitative (>95%) yield as colourless to light-brown low-melting plates, which are very soluble in water. Single crystals suitable for X-ray structure analysis were obtained by slow evaporation of a concentrated aqueous solution at room temperature. IR: 3372 (*s br*), 3226 (*sh br*), 2985 (*m*), 2949 (*m*), 2875 (*w*), 1641 (*sh*), 1603 (*sh*), 1587 (*s*), 1497 (*s*), 1443 (*s*), 1374 (*s*), 1338 (*m*), 1316 (*w*), 1290 (*s*), 1257 (*m*), 1230 (*w*), 1176 (*m*), 1155 (*s*), 1083 (*w*), 1050 (*w*), 1003 (*m*), 948 (*m*), 918 (*m*), 899 (*w*), 846 (*m*), 794 (*m*), 666 (*s br*), 562 (*s*), 479 (*s*), 446 (*m*)  $cm^{-1}$ .  $^1H$  NMR [400 MHz,  $D_2O$ , 298 (2) K]:  $\delta$  1.89–1.98 (3  $\times$  *m*, 3H; 3- $CH_2$  + 4- $CH_2$ ), 2.24 (*m*, 1H; 3- $CH_2$ ),

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$[K_2(C_6H_7NO_2S_2)(H_2O)_3]$
$M_r$	321.49
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	153
$a, b, c$ (Å)	7.1700 (3), 8.9723 (4), 19.8379 (7)
$V$ (Å <sup>3</sup> )	1276.20 (9)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	1.07
Crystal size (mm)	0.44 $\times$ 0.10 $\times$ 0.07
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Numerical ( <i>X-AREA</i> and <i>X-RED</i> ; Stoe & Cie, 2002)
$T_{min}, T_{max}$	0.741, 0.935
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	8831, 2794, 2511
$R_{int}$	0.038
$(\sin \theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.042, 0.97
No. of reflections	2794
No. of parameters	164
No. of restraints	6
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.25, -0.22
Absolute structure	Flack $x$ determined using 979 quotients $[(I^+) - (I^-)] /$ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.00 (4)

Computer programs: *X-AREA* (Stoe & Cie, 2002), *X-RED* (Stoe & Cie, 2002), *SIR97* (Altomare *et al.*, 1999), *SHELXL2016* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

3.75 (*m*, 1H; 5- $CH_2$ ), 3.83 (*m*, 1H; 5- $CH_2$ ), 4.72 (*dd*,  $J_1 = 8.7, J_2 = 3.2$  Hz, 1H; 2- $CH$ ).  $^{13}C$  NMR [100 MHz,  $D_2O$ , 298 (2) K]:  $\delta$  24.6 (4- $CH_2$ ), 31.5 (3- $CH_2$ ), 55.7 (5- $CH_2$ ), 69.5 (2- $CH$ ), 179.9 (COO), 205.8 (CSS).



**Figure 5**  
The supramolecular layer illustrated in Fig. 4, viewed in a projection on (010).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. H atoms on C atoms were fixed geometrically and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . C–H distances within the CH<sub>2</sub> groups were constrained to 0.99 Å and that within the CH group to 1.00 Å. The water H-atom sites were located in difference Fourier maps and refined using restraints on the O–H distance [target value = 0.84 (2) Å]. The corresponding  $U_{\text{iso}}(\text{H})$  values were set at  $1.5U_{\text{eq}}(\text{O})$ . The reflection (002) disagreed strongly with the structural model and was therefore omitted from the refinement.

## Acknowledgements

General financial support of this work by the Otto-von-Guericke-Universität Magdeburg, Germany, is gratefully acknowledged.

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## supporting information

*Acta Cryst.* (2017). E73, 1375-1378 [https://doi.org/10.1107/S2056989017011999]

Crystal structure of dipotassium *N*-carbodithioato-L-prolinate trihydrate

Phil Liebing

## Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-AREA* and *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Poly[tri- $\mu$ -aqua-( $\mu$ -2-carboxylatopyrrolidine-1-carbodithioato)dipotassium]

## Crystal data

$[\text{K}_2(\text{C}_6\text{H}_7\text{NO}_2\text{S}_2)(\text{H}_2\text{O})_3]$

$M_r = 321.49$

Orthorhombic,  $P2_12_12_1$

$a = 7.1700$  (3) Å

$b = 8.9723$  (4) Å

$c = 19.8379$  (7) Å

$V = 1276.20$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 664$

$D_x = 1.673$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 10736 reflections

$\theta = 2.5\text{--}29.2^\circ$

$\mu = 1.07$  mm<sup>-1</sup>

$T = 153$  K

Plate, colorless

$0.44 \times 0.10 \times 0.07$  mm

## Data collection

Stoe IPDS 2T  
diffractometer

Radiation source: fine-focus sealed tube

Detector resolution: 6.67 pixels mm<sup>-1</sup>

$\omega$  scan

Absorption correction: numerical  
(*X-AREA* and *X-RED*; Stoe & Cie, 2002)

$T_{\min} = 0.741$ ,  $T_{\max} = 0.935$

8831 measured reflections

2794 independent reflections

2511 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.0^\circ$ ,  $\theta_{\min} = 2.5^\circ$

$h = -9 \rightarrow 9$

$k = -11 \rightarrow 11$

$l = -22 \rightarrow 25$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.042$

$S = 0.97$

2794 reflections

164 parameters

6 restraints

Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.25$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.22$  e Å<sup>-3</sup>

Extinction correction: SHELXL2016

(Sheldrick, 2015),

$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0051 (7)



Absolute structure: Flack  $x$  determined using  
 979 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)  
 Absolute structure parameter: 0.00 (4)

### 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.0231 (3)	0.2133 (3)	0.89993 (13)	0.0120 (5)
C2	-0.0116 (3)	0.3153 (3)	0.83918 (13)	0.0103 (5)
H1	-0.098814	0.397715	0.851816	0.012*
C3	0.2180 (4)	0.3035 (3)	0.74906 (14)	0.0140 (6)
H3	0.348536	0.268134	0.751636	0.017*
H2	0.205712	0.372618	0.710395	0.017*
C4	0.0837 (4)	0.1734 (3)	0.74238 (15)	0.0157 (6)
H5	0.135307	0.082539	0.763649	0.019*
H4	0.056006	0.152175	0.694439	0.019*
C5	-0.0907 (4)	0.2267 (3)	0.77943 (14)	0.0156 (6)
H6	-0.166526	0.141324	0.795180	0.019*
H7	-0.168314	0.290872	0.750111	0.019*
C6	0.2657 (3)	0.4759 (3)	0.84517 (12)	0.0098 (5)
N	0.1619 (3)	0.3766 (2)	0.81226 (11)	0.0092 (4)
O1	0.1821 (2)	0.1556 (2)	0.90730 (10)	0.0157 (4)
O2	-0.1122 (2)	0.1894 (2)	0.93751 (12)	0.0207 (4)
O3	0.7663 (3)	0.5383 (3)	0.98964 (10)	0.0217 (4)
H8	0.856 (4)	0.512 (4)	0.9680 (15)	0.033*
H9	0.747 (4)	0.471 (4)	1.0179 (15)	0.033*
O4	0.9025 (3)	0.8561 (2)	0.92654 (13)	0.0280 (5)
H10	0.999 (4)	0.821 (4)	0.912 (2)	0.042*
H11	0.914 (5)	0.943 (3)	0.934 (2)	0.042*
O5	0.4779 (3)	0.0059 (2)	0.85399 (10)	0.0240 (5)
H13	0.373 (3)	0.038 (4)	0.8575 (18)	0.036*
H12	0.505 (4)	-0.005 (4)	0.8144 (12)	0.036*
K1	0.53230 (8)	0.28003 (6)	0.93500 (3)	0.01712 (14)
K2	0.54335 (7)	0.76029 (6)	0.93744 (3)	0.01595 (13)
S1	0.47870 (8)	0.52667 (8)	0.81344 (3)	0.01487 (14)
S2	0.18705 (8)	0.54540 (7)	0.92079 (3)	0.01487 (15)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0121 (11)	0.0107 (12)	0.0133 (13)	-0.0024 (9)	-0.0008 (10)	-0.0016 (9)
C2	0.0068 (11)	0.0108 (11)	0.0134 (13)	0.0003 (9)	-0.0006 (10)	0.0007 (9)

C3	0.0154 (14)	0.0153 (13)	0.0112 (14)	-0.0017 (10)	0.0030 (10)	-0.0030 (11)
C4	0.0192 (14)	0.0133 (13)	0.0145 (15)	-0.0047 (10)	-0.0023 (10)	-0.0031 (11)
C5	0.0151 (12)	0.0151 (14)	0.0167 (15)	-0.0028 (10)	-0.0038 (10)	-0.0007 (11)
C6	0.0097 (10)	0.0096 (11)	0.0100 (12)	0.0016 (10)	-0.0005 (8)	0.0021 (11)
N	0.0095 (9)	0.0086 (10)	0.0096 (11)	-0.0024 (8)	-0.0003 (8)	-0.0004 (8)
O1	0.0135 (8)	0.0164 (9)	0.0171 (11)	0.0057 (8)	0.0000 (8)	0.0034 (8)
O2	0.0127 (8)	0.0312 (12)	0.0183 (11)	-0.0002 (7)	0.0040 (9)	0.0082 (10)
O3	0.0206 (9)	0.0208 (10)	0.0237 (11)	0.0048 (8)	0.0084 (8)	0.0098 (10)
O4	0.0223 (10)	0.0214 (11)	0.0403 (16)	-0.0048 (8)	0.0009 (10)	-0.0010 (12)
O5	0.0233 (9)	0.0330 (13)	0.0158 (10)	0.0126 (9)	0.0033 (8)	0.0009 (9)
K1	0.0115 (2)	0.0201 (3)	0.0197 (3)	0.0003 (2)	-0.0003 (3)	0.0014 (2)
K2	0.0146 (3)	0.0140 (3)	0.0192 (3)	-0.0005 (2)	-0.0023 (3)	-0.0006 (2)
S1	0.0125 (3)	0.0187 (3)	0.0134 (3)	-0.0058 (3)	0.0023 (2)	-0.0005 (3)
S2	0.0135 (3)	0.0182 (3)	0.0129 (3)	-0.0022 (3)	0.0020 (2)	-0.0062 (3)

*Geometric parameters (Å, °)*

C1—O2	1.242 (3)	O3—K1	3.060 (2)
C1—O1	1.261 (3)	O3—H8	0.81 (2)
C1—C2	1.533 (4)	O3—H9	0.83 (2)
C1—K1 <sup>i</sup>	3.276 (3)	O4—K2	2.723 (2)
C2—N	1.462 (3)	O4—K2 <sup>iii</sup>	3.065 (3)
C2—C5	1.536 (4)	O4—H10	0.81 (2)
C2—H1	1.0000	O4—H11	0.80 (2)
C3—N	1.471 (3)	O5—K2 <sup>iv</sup>	2.796 (2)
C3—C4	1.519 (4)	O5—K1	2.964 (2)
C3—H3	0.9900	O5—H13	0.81 (2)
C3—H2	0.9900	O5—H12	0.81 (2)
C4—C5	1.527 (4)	K1—O2 <sup>v</sup>	2.6758 (19)
C4—H5	0.9900	K1—O2 <sup>vi</sup>	2.747 (2)
C4—H4	0.9900	K1—C1 <sup>vi</sup>	3.276 (3)
C5—H6	0.9900	K1—S1	3.2956 (9)
C5—H7	0.9900	K1—O1 <sup>vi</sup>	3.358 (2)
C6—N	1.332 (3)	K1—S2	3.4463 (8)
C6—S1	1.714 (2)	K1—H9	2.83 (4)
C6—S2	1.719 (3)	K1—H13	2.90 (4)
C6—K1	3.150 (2)	K2—O5 <sup>vii</sup>	2.796 (2)
O1—K1	2.8023 (19)	K2—O3 <sup>viii</sup>	3.050 (2)
O1—K1 <sup>i</sup>	3.358 (2)	K2—O4 <sup>viii</sup>	3.065 (3)
O2—K1 <sup>ii</sup>	2.6758 (19)	K2—S2	3.2176 (8)
O2—K1 <sup>i</sup>	2.747 (2)	K2—S1	3.2650 (9)
O3—K2	2.756 (2)	K2—S2 <sup>iii</sup>	3.4656 (9)
O3—K2 <sup>iii</sup>	3.050 (2)	S2—K2 <sup>viii</sup>	3.4656 (9)
O2—C1—O1	124.5 (2)	C6—K1—K2	57.29 (5)
O2—C1—C2	116.6 (2)	C1 <sup>vi</sup> —K1—K2	88.33 (4)
O1—C1—C2	118.9 (2)	S1—K1—K2	48.625 (16)
O2—C1—K1 <sup>i</sup>	54.47 (14)	O1 <sup>vi</sup> —K1—K2	79.14 (4)

O1—C1—K1 <sup>i</sup>	82.72 (15)	S2—K1—K2	47.420 (14)
C2—C1—K1 <sup>i</sup>	141.07 (16)	O2 <sup>v</sup> —K1—K1 <sup>vi</sup>	35.39 (5)
N—C2—C1	111.93 (19)	O2 <sup>vi</sup> —K1—K1 <sup>vi</sup>	77.43 (4)
N—C2—C5	103.1 (2)	O1—K1—K1 <sup>vi</sup>	141.94 (4)
C1—C2—C5	110.9 (2)	O5—K1—K1 <sup>vi</sup>	108.66 (4)
N—C2—H1	110.2	O3—K1—K1 <sup>vi</sup>	56.26 (4)
C1—C2—H1	110.2	C6—K1—K1 <sup>vi</sup>	152.21 (5)
C5—C2—H1	110.2	C1 <sup>vi</sup> —K1—K1 <sup>vi</sup>	55.88 (5)
N—C3—C4	104.1 (2)	S1—K1—K1 <sup>vi</sup>	126.83 (2)
N—C3—H3	110.9	O1 <sup>vi</sup> —K1—K1 <sup>vi</sup>	39.01 (3)
C4—C3—H3	110.9	S2—K1—K1 <sup>vi</sup>	135.23 (3)
N—C3—H2	110.9	K2—K1—K1 <sup>vi</sup>	95.725 (18)
C4—C3—H2	110.9	O2 <sup>v</sup> —K1—H9	69.9 (7)
H3—C3—H2	109.0	O2 <sup>vi</sup> —K1—H9	67.0 (6)
C3—C4—C5	103.7 (2)	O1—K1—H9	147.4 (6)
C3—C4—H5	111.0	O5—K1—H9	152.8 (7)
C5—C4—H5	111.0	O3—K1—H9	15.6 (5)
C3—C4—H4	111.0	C6—K1—H9	108.6 (6)
C5—C4—H4	111.0	C1 <sup>vi</sup> —K1—H9	54.5 (5)
H5—C4—H4	109.0	S1—K1—H9	94.6 (5)
C4—C5—C2	103.4 (2)	O1 <sup>vi</sup> —K1—H9	35.0 (5)
C4—C5—H6	111.1	S2—K1—H9	91.1 (6)
C2—C5—H6	111.1	K2—K1—H9	51.5 (6)
C4—C5—H7	111.1	K1 <sup>vi</sup> —K1—H9	45.5 (6)
C2—C5—H7	111.1	O2 <sup>v</sup> —K1—H13	99.1 (5)
H6—C5—H7	109.0	O2 <sup>vi</sup> —K1—H13	114.5 (7)
N—C6—S1	119.70 (18)	O1—K1—H13	40.8 (5)
N—C6—S2	119.16 (17)	O5—K1—H13	15.8 (4)
S1—C6—S2	121.09 (15)	O3—K1—H13	166.5 (6)
N—C6—K1	104.05 (16)	C6—K1—H13	83.0 (6)
S1—C6—K1	79.34 (8)	C1 <sup>vi</sup> —K1—H13	122.4 (7)
S2—C6—K1	84.71 (9)	S1—K1—H13	94.0 (7)
C6—N—C2	123.2 (2)	O1 <sup>vi</sup> —K1—H13	138.6 (7)
C6—N—C3	124.3 (2)	S2—K1—H13	101.0 (5)
C2—N—C3	112.12 (18)	K2—K1—H13	139.7 (7)
C1—O1—K1	132.01 (16)	K1 <sup>vi</sup> —K1—H13	122.3 (6)
C1—O1—K1 <sup>i</sup>	75.41 (15)	H9—K1—H13	167.8 (8)
K1—O1—K1 <sup>i</sup>	92.03 (5)	O4—K2—O3	73.12 (7)
C1—O2—K1 <sup>ii</sup>	132.87 (17)	O4—K2—O5 <sup>vii</sup>	82.11 (7)
C1—O2—K1 <sup>i</sup>	103.94 (16)	O3—K2—O5 <sup>vii</sup>	152.81 (6)
K1 <sup>ii</sup> —O2—K1 <sup>i</sup>	110.25 (8)	O4—K2—O3 <sup>viii</sup>	117.80 (6)
K2—O3—K2 <sup>iii</sup>	97.35 (7)	O3—K2—O3 <sup>viii</sup>	128.88 (4)
K2—O3—K1	95.52 (6)	O5 <sup>vii</sup> —K2—O3 <sup>viii</sup>	72.82 (6)
K2 <sup>iii</sup> —O3—K1	166.87 (8)	O4—K2—O4 <sup>viii</sup>	119.29 (6)
K2—O3—H8	118 (2)	O3—K2—O4 <sup>viii</sup>	67.29 (6)
K2 <sup>iii</sup> —O3—H8	85 (3)	O5 <sup>vii</sup> —K2—O4 <sup>viii</sup>	137.28 (6)
K1—O3—H8	92 (3)	O3 <sup>viii</sup> —K2—O4 <sup>viii</sup>	64.51 (6)
K2—O3—H9	133 (2)	O4—K2—S2	158.71 (6)



K2 <sup>iii</sup> —O3—H9	103 (2)	O3—K2—S2	93.79 (5)
K1—O3—H9	66 (2)	O5 <sup>vii</sup> —K2—S2	106.15 (5)
H8—O3—H9	106 (3)	O3 <sup>viii</sup> —K2—S2	83.48 (4)
K2—O4—K2 <sup>iii</sup>	97.70 (8)	O4 <sup>viii</sup> —K2—S2	67.94 (5)
K2—O4—H10	135 (3)	O4—K2—S1	106.09 (6)
K2 <sup>iii</sup> —O4—H10	84 (3)	O3—K2—S1	84.35 (5)
K2—O4—H11	113 (2)	O5 <sup>vii</sup> —K2—S1	92.06 (5)
K2 <sup>iii</sup> —O4—H11	98 (3)	O3 <sup>viii</sup> —K2—S1	130.18 (4)
H10—O4—H11	111 (4)	O4 <sup>viii</sup> —K2—S1	113.44 (5)
K2 <sup>iv</sup> —O5—K1	108.11 (6)	S2—K2—S1	54.915 (17)
K2 <sup>iv</sup> —O5—H13	113 (3)	O4—K2—S2 <sup>iii</sup>	67.95 (6)
K1—O5—H13	77 (3)	O3—K2—S2 <sup>iii</sup>	83.46 (5)
K2 <sup>iv</sup> —O5—H12	116 (3)	O5 <sup>vii</sup> —K2—S2 <sup>iii</sup>	97.70 (5)
K1—O5—H12	126 (3)	O3 <sup>viii</sup> —K2—S2 <sup>iii</sup>	60.71 (4)
H13—O5—H12	110 (3)	O4 <sup>viii</sup> —K2—S2 <sup>iii</sup>	63.57 (5)
O2 <sup>v</sup> —K1—O2 <sup>vi</sup>	111.87 (5)	S2—K2—S2 <sup>iii</sup>	128.38 (2)
O2 <sup>v</sup> —K1—O1	137.40 (6)	S1—K2—S2 <sup>iii</sup>	167.58 (2)
O2 <sup>vi</sup> —K1—O1	83.24 (6)	O4—K2—K1	109.40 (5)
O2 <sup>v</sup> —K1—O5	83.31 (6)	O3—K2—K1	44.96 (5)
O2 <sup>vi</sup> —K1—O5	122.17 (6)	O5 <sup>vii</sup> —K2—K1	141.10 (5)
O1—K1—O5	56.29 (5)	O3 <sup>viii</sup> —K2—K1	125.84 (4)
O2 <sup>v</sup> —K1—O3	72.61 (6)	O4 <sup>viii</sup> —K2—K1	70.31 (4)
O2 <sup>vi</sup> —K1—O3	78.76 (6)	S2—K2—K1	52.061 (16)
O1—K1—O3	149.61 (6)	S1—K2—K1	49.238 (17)
O5—K1—O3	153.24 (6)	S2 <sup>iii</sup> —K2—K1	121.17 (2)
O2 <sup>v</sup> —K1—C6	139.31 (7)	O4—K2—K2 <sup>iii</sup>	44.10 (5)
O2 <sup>vi</sup> —K1—C6	103.67 (6)	O3—K2—K2 <sup>iii</sup>	43.88 (5)
O1—K1—C6	64.38 (6)	O5 <sup>vii</sup> —K2—K2 <sup>iii</sup>	120.53 (5)
O5—K1—C6	94.38 (6)	O3 <sup>viii</sup> —K2—K2 <sup>iii</sup>	106.88 (4)
O3—K1—C6	96.35 (6)	O4 <sup>viii</sup> —K2—K2 <sup>iii</sup>	75.86 (5)
O2 <sup>v</sup> —K1—C1 <sup>vi</sup>	90.35 (7)	S2—K2—K2 <sup>iii</sup>	133.26 (3)
O2 <sup>vi</sup> —K1—C1 <sup>vi</sup>	21.59 (6)	S1—K2—K2 <sup>iii</sup>	121.19 (2)
O1—K1—C1 <sup>vi</sup>	100.67 (6)	S2 <sup>iii</sup> —K2—K2 <sup>iii</sup>	46.809 (17)
O5—K1—C1 <sup>vi</sup>	123.68 (6)	K1—K2—K2 <sup>iii</sup>	88.808 (18)
O3—K1—C1 <sup>vi</sup>	69.09 (6)	O4—K2—K2 <sup>viii</sup>	146.64 (6)
C6—K1—C1 <sup>vi</sup>	122.90 (6)	O3—K2—K2 <sup>viii</sup>	103.43 (5)
O2 <sup>v</sup> —K1—S1	109.19 (5)	O5 <sup>vii</sup> —K2—K2 <sup>viii</sup>	103.43 (4)
O2 <sup>vi</sup> —K1—S1	124.25 (4)	O3 <sup>viii</sup> —K2—K2 <sup>viii</sup>	38.77 (4)
O1—K1—S1	91.12 (4)	O4 <sup>viii</sup> —K2—K2 <sup>viii</sup>	38.20 (4)
O5—K1—S1	98.34 (4)	S2—K2—K2 <sup>viii</sup>	51.744 (13)
O3—K1—S1	79.31 (4)	S1—K2—K2 <sup>viii</sup>	106.540 (19)
C6—K1—S1	30.73 (4)	S2 <sup>iii</sup> —K2—K2 <sup>viii</sup>	78.70 (2)
C1 <sup>vi</sup> —K1—S1	135.80 (5)	K1—K2—K2 <sup>viii</sup>	87.075 (19)
O2 <sup>v</sup> —K1—O1 <sup>vi</sup>	74.35 (6)	K2 <sup>iii</sup> —K2—K2 <sup>viii</sup>	110.46 (3)
O2 <sup>vi</sup> —K1—O1 <sup>vi</sup>	41.03 (5)	O4—K2—K1 <sup>vii</sup>	72.51 (5)
O1—K1—O1 <sup>vi</sup>	122.54 (5)	O3—K2—K1 <sup>vii</sup>	137.42 (5)
O5—K1—O1 <sup>vi</sup>	133.64 (5)	O5 <sup>vii</sup> —K2—K1 <sup>vii</sup>	37.15 (4)
O3—K1—O1 <sup>vi</sup>	50.52 (5)	O3 <sup>viii</sup> —K2—K1 <sup>vii</sup>	53.25 (4)

C6—K1—O1 <sup>vi</sup>	128.70 (6)	O4 <sup>viii</sup> —K2—K1 <sup>vii</sup>	110.14 (5)
C1 <sup>vi</sup> —K1—O1 <sup>vi</sup>	21.87 (5)	S2—K2—K1 <sup>vii</sup>	125.77 (2)
S1—K1—O1 <sup>vi</sup>	127.12 (4)	S1—K2—K1 <sup>vii</sup>	129.17 (2)
O2 <sup>v</sup> —K1—S2	153.59 (5)	S2 <sup>iii</sup> —K2—K1 <sup>vii</sup>	60.694 (17)
O2 <sup>vi</sup> —K1—S2	74.66 (4)	K1—K2—K1 <sup>vii</sup>	177.62 (2)
O1—K1—S2	67.40 (4)	K2 <sup>iii</sup> —K2—K1 <sup>vii</sup>	93.565 (18)
O5—K1—S2	115.75 (4)	K2 <sup>viii</sup> —K2—K1 <sup>vii</sup>	91.962 (18)
O3—K1—S2	84.23 (4)	C6—S1—K2	91.16 (9)
C6—K1—S2	29.79 (5)	C6—S1—K1	69.92 (8)
C1 <sup>vi</sup> —K1—S2	93.14 (5)	K2—S1—K1	82.14 (2)
S1—K1—S2	52.585 (17)	C6—S2—K2	92.67 (8)
O1 <sup>vi</sup> —K1—S2	100.79 (4)	C6—S2—K1	65.51 (8)
O2 <sup>v</sup> —K1—K2	106.61 (4)	K2—S2—K1	80.519 (19)
O2 <sup>vi</sup> —K1—K2	84.08 (4)	C6—S2—K2 <sup>viii</sup>	171.04 (10)
O1—K1—K2	114.65 (4)	K2—S2—K2 <sup>viii</sup>	81.447 (18)
O5—K1—K2	146.95 (4)	K1—S2—K2 <sup>viii</sup>	119.65 (2)
O3—K1—K2	39.52 (4)		
O2—C1—C2—N	160.5 (2)	C4—C3—N—C2	-8.5 (3)
O1—C1—C2—N	-21.9 (3)	O2—C1—O1—K1	-116.4 (2)
K1 <sup>i</sup> —C1—C2—N	95.0 (3)	C2—C1—O1—K1	66.3 (3)
O2—C1—C2—C5	-84.9 (3)	K1 <sup>i</sup> —C1—O1—K1	-79.32 (18)
O1—C1—C2—C5	92.6 (3)	O2—C1—O1—K1 <sup>i</sup>	-37.0 (2)
K1 <sup>i</sup> —C1—C2—C5	-150.4 (2)	C2—C1—O1—K1 <sup>i</sup>	145.6 (2)
N—C3—C4—C5	28.1 (3)	O1—C1—O2—K1 <sup>ii</sup>	-176.93 (17)
C3—C4—C5—C2	-37.1 (3)	C2—C1—O2—K1 <sup>ii</sup>	0.5 (3)
N—C2—C5—C4	31.5 (3)	K1 <sup>i</sup> —C1—O2—K1 <sup>ii</sup>	135.8 (2)
C1—C2—C5—C4	-88.5 (3)	O1—C1—O2—K1 <sup>i</sup>	47.3 (3)
S1—C6—N—C2	173.28 (17)	C2—C1—O2—K1 <sup>i</sup>	-135.35 (18)
S2—C6—N—C2	-4.1 (3)	N—C6—S1—K2	178.61 (19)
K1—C6—N—C2	87.7 (2)	S2—C6—S1—K2	-4.09 (15)
S1—C6—N—C3	0.5 (3)	K1—C6—S1—K2	-81.19 (4)
S2—C6—N—C3	-176.82 (19)	N—C6—S1—K1	-100.2 (2)
K1—C6—N—C3	-85.1 (2)	S2—C6—S1—K1	77.11 (14)
C1—C2—N—C6	-68.8 (3)	N—C6—S2—K2	-178.53 (19)
C5—C2—N—C6	171.9 (2)	S1—C6—S2—K2	4.15 (15)
C1—C2—N—C3	104.8 (2)	K1—C6—S2—K2	78.32 (4)
C5—C2—N—C3	-14.5 (3)	N—C6—S2—K1	103.2 (2)
C4—C3—N—C6	165.0 (2)	S1—C6—S2—K1	-74.17 (14)

Symmetry codes: (i)  $x-1/2, -y+1/2, -z+2$ ; (ii)  $x-1, y, z$ ; (iii)  $x+1/2, -y+3/2, -z+2$ ; (iv)  $x, y-1, z$ ; (v)  $x+1, y, z$ ; (vi)  $x+1/2, -y+1/2, -z+2$ ; (vii)  $x, y+1, z$ ; (viii)  $x-1/2, -y+3/2, -z+2$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H9 $\cdots$ O1 <sup>vi</sup>	0.83 (2)	1.93 (2)	2.752 (3)	170 (4)
O3—H8 $\cdots$ S2 <sup>v</sup>	0.81 (2)	2.57 (2)	3.3123 (19)	153 (3)
O4—H11 $\cdots$ O2 <sup>ix</sup>	0.80 (2)	2.22 (2)	3.000 (3)	166 (4)

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O5—H13···O1	0.81 (2)	1.99 (3)	2.724 (3)	150 (3)
O5—H12···S1 <sup>*</sup>	0.81 (2)	2.55 (2)	3.341 (2)	163 (3)

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Symmetry codes: (v)  $x+1, y, z$ ; (vi)  $x+1/2, -y+1/2, -z+2$ ; (ix)  $x+1, y+1, z$ ; (x)  $-x+1, y-1/2, -z+3/2$ .