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A new tetrakis-substituted pyrazine carboxylic acid, 3,3′,3″,3‴-{[pyrazine-2,3,5,6-tetrayltetrakis-(methylene)]tetrakis(sulfanediyl)}tetrapropionic acid: crystal structures of two triclinic polymorphs and of two potassium–organic frameworks

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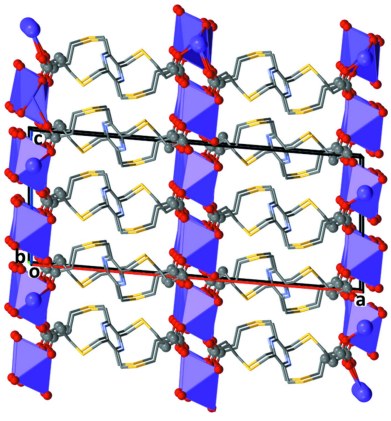
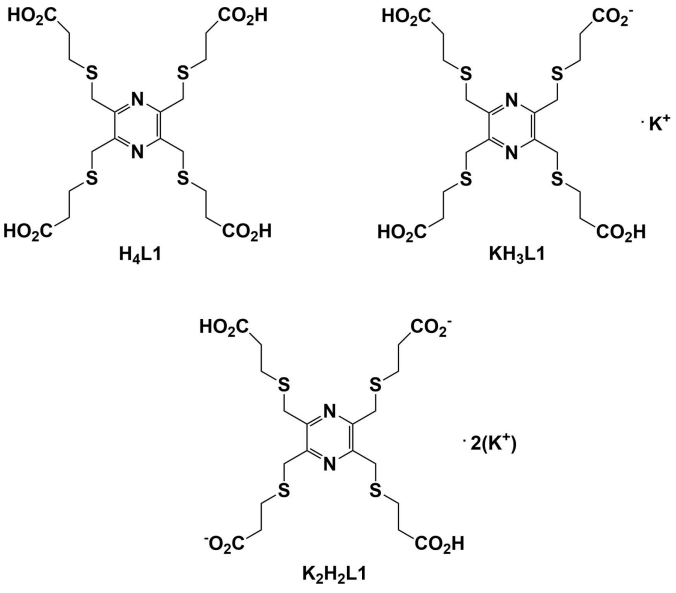
Two polymorphs of the title tetrakis-substituted pyrazine carboxylic acid, 3,3′,3″,3‴-{[pyrazine-2,3,5,6-tetrayltetrakis(methylene))tetrakis(sulfanediyl]}-tetrapropionic acid, $C_{20}H_{28}N_2O_8S_4$, (**H_4L1**), have been obtained, **H_4L1_A** and **H_4L1_B**. Each structure crystallized with half a molecule in the asymmetric unit of a triclinic $P\overline{1}$ unit cell. The whole molecules are generated by inversion symmetry, with the pyrazine rings being located about inversion centers. The crystals of **H_4L1_B** were of poor quality, but the X-ray diffraction analysis does show the change in conformation of the –CH_2—S—CH_2—CH_2– side chains compared to those in polymorph **H_4L1_A**. In the crystal of **H_4L1_A**, molecules are linked by two pairs of O—H···O hydrogen bonds, enclosing $R_2^2(8)$ ring motifs forming layers parallel to plane (100), which are linked by C—H···O hydrogen bonds to form a supramolecular framework. In the crystal of **H_4L1_B**, molecules are also linked by two pairs of O—H···O hydrogen bonds enclosing $R_2^2(8)$ ring motifs, however here, chains are formed propagating in the [001] direction and stacking up the *a*-axis. Reaction of **H_4L1** with $Hg(NO_3)_2$ in the presence of a potassium acetate buffer did not produce the expected binuclear complex, instead crystals of a potassium–organic framework were obtained, poly[(μ-3-{[(3,5,6-tris{[(2-carboxyethyl)sulfanyl]methyl}pyrazin-2-yl)methyl]-sulfanyl}propanoato)potassium], $[K(C_{20}H_{27}N_2O_8S_4)]_n$ (**KH_3L1**). The organic mono-anion possesses inversion symmetry with the pyrazine ring being located about an inversion center. A carboxy H atom is disordered by symmetry and the charge is compensated for by a potassium ion. A similar reaction with $Zn(NO_3)_2$ resulted in the formation of crystals of a dipotassium-organic framework, poly[(μ-3,3′-{[(3,6-bis{[(2-carboxyethyl)sulfanyl]methyl}pyrazine-2,5-diyl)bis-(methylene)]bis(sulfanediyl)}dipropionato)dipotassium], $[K_2(C_{20}H_{26}N_2O_8S_4)]_n$ (**K_2H_2L1**). Here, the organic di-anion possesses inversion symmetry with the pyrazine ring being located about an inversion center. Two symmetry-related acid groups are deprotonated and the charges are compensated for by two potassium ions.



1. Chemical context

The title tetrakis-substituted pyrazine carboxylic acid, 3,3′,3″,3‴-[(pyrazine-2,3,5,6-tetrayltetrakis(methylene))tetrakis(sulfanediyl)]tetrapropionic acid (**H_4L1**), is to the best of our knowledge, only the third pyrazine tetrakis-substituted carboxylic acid ligand to have been synthesized. The first is pyrazine-2,3,5,6-tetracarboxylic acid (**pztca**), which was originally synthesized by Wolff at the end of the 19th century (Wolff, 1887, 1893), while the second is 4,4′,4″,4‴-(pyrazine-2,3,5,6-tetrayl)tetrabenzoic acid (**pztba**), which was first

synthesized by Jiang *et al.* (2017). **Pztca** (Fig. 1) has been used to synthesize a number of coordination polymers, the first being poly{[(2,5-dicarboxypyrazine-3,6-dicarboxylato)-transdiaquairon(II) dihydrate]} (Marioni *et al.*, 1986), while **pztba** (Fig. 1) has been shown to form a series of metal–organic frameworks (Jiang *et al.*, 2017; Wang *et al.*, 2019).



The title ligand was synthesized to study its coordination behaviour with various transition metal ions (Pacifico, 2003). Potentially the ligand can coordinate in a bis-pentadentate manner, as was shown to be the case for a similar ligand, 2,2′,2″,2‴-{[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(sulfanediyl)}tetrakis(ethan-1-amine) (**H$_4$L2**), for which two nickel(II) binuclear complexes, **I** and **II**, were synthesized (Pacifico, 2003; Pacifico & Stoeckli-Evans, 2020); see Fig. 2.

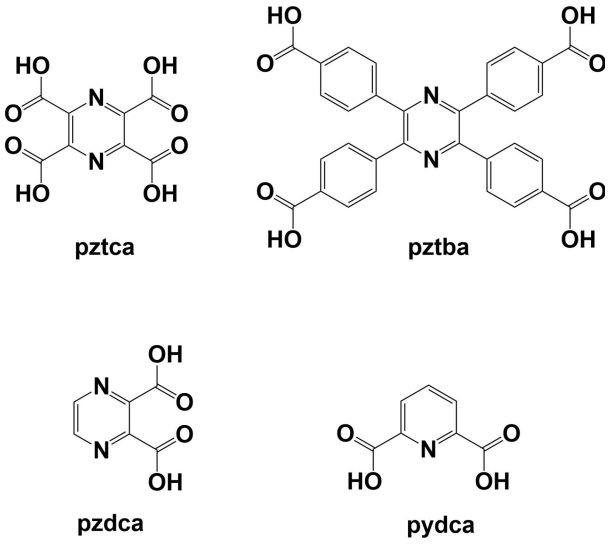


Figure 1
Chemical diagrams for pyrazine-2,3,5,6-tetracarboxylic acid (**pztca**), 4,4′,4″,4‴-(pyrazine-2,3,5,6-tetrayl)tetrabenzoic acid (**pztba**), pyrazine-2,3-dicarboxylic acid (**pzdca**) and pyridine-2,6-dicarboxylic acid (**pydca**).

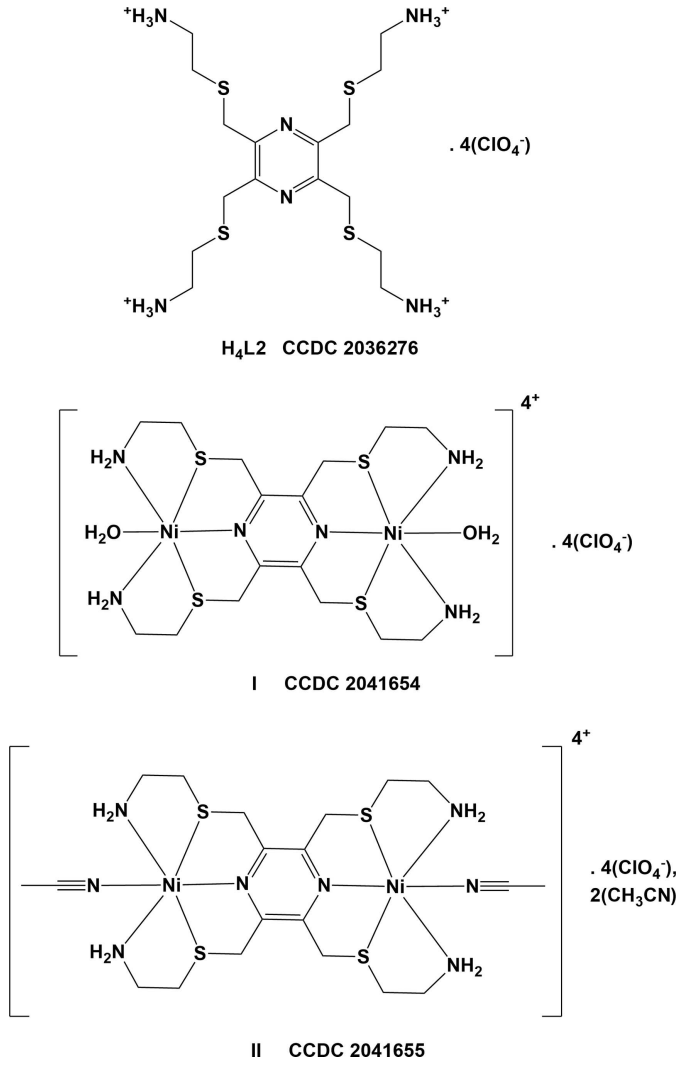


Figure 2
Chemical diagram for 2,2′,2″,2‴-[(pyrazine-2,3,5,6-tetrayltetrakis-(methylene)tetrakis(sulfanediyl)]tetrakis(ethan-1-amine) (**H$_4$L2**) and two nickel(II) binuclear complexes, **I** and **II** (Pacifico & Stoeckli-Evans, 2020).

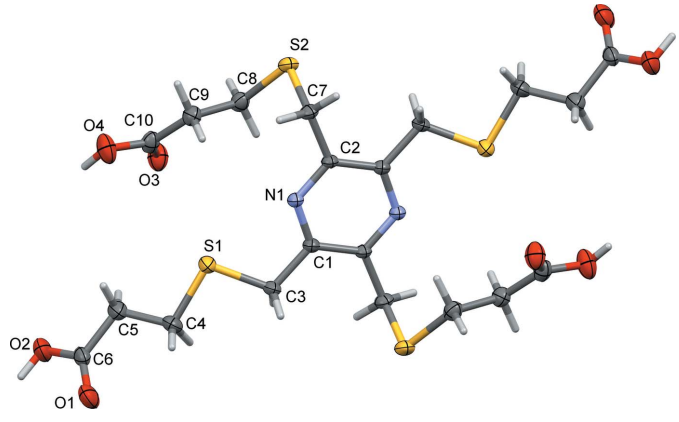


Figure 3
The molecular structure of **H$_4$L1_A**, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by symmetry operator $-x + 2, -y + 1, -z + 1$.

Table 1
Selected torsion angles (°) along the $C_{ar}—CH_2—S—CH_2—CH_2—CO_2H$ side chains in compounds **H_4L1_A**, **H_4L1_B**, **KH_3L1** and **K_2H_2L1**.

Torsion angle	**H_4L1_A**	**H_4L1_B**	**KH_3L1**	**K_2H_2L1**
C1—C3—S1—C4	174.1 (2)	−72.6 (4)	−72.32)	−65.81 (15)
C3—S1—C4—C5	−155.3 (2)	−86.7 (4)	−90.3 (2)	−87.72 (15)
S1—C4—C5—C6	−167.9 (2)	−65.0 (6)	−76.4 (3)	−73.19 (18)
C2—C7—S2—C8	57.6 (2)	−66.8 (4)	−62.3 (2)	−67.34 (15)
C7—S2—C8—C9	65.7 (2)	−178.1 (5)	−77.5 (2)	97.89 (15)
S2—C8—C9—C10	174.8 (2)	−172.5 (5)	−173.8 (2)	174.51 (12)

2. Structural commentary

The title tetrakis-substituted pyrazine carboxylic acid, 3,3′,3″,3‴-[(pyrazine-2,3,5,6-tetrayltetrakis(methylene))tetrakis(sulfanediyl)]tetrapropionic acid (**H_4L1_A**), crystallized with half a molecule in the asymmetric unit (Fig. 3). The whole molecule is generated by inversion symmetry, with the pyrazine ring being located about an inversion center.

In an attempt to form a co-crystal, equimolar amounts of **H_4L1** and terephthalic acid were mixed in methanol. On slow evaporation of the solvent, colourless plate-like crystals were obtained. X-ray diffraction analysis revealed their structure to be that of a second triclinic $P\overline{1}$ polymorph, **H_4L1_B** (Fig. 4). It crystallized with half a molecule in the asymmetric unit and the whole molecule is generated by inversion symmetry, with the pyrazine ring being located about an inversion center. The crystals were of poor quality with one $CH_2—CH_2—CO_2H$ side chain (atoms C8/C8*B*, C9/C9*B*, C10/C10*B*, O3/O3*B*, O4/O4*B*) of the centrosymmetric molecule being positionally disordered (Fig. 4*b*). The difference in the two polymorphs is essentially in the orientation of the $–CH_2—S—CH_2—CH_2—C–$ side arms, as shown in Fig. 5*a* and *b*. Selected torsion angles are given in Table 1.

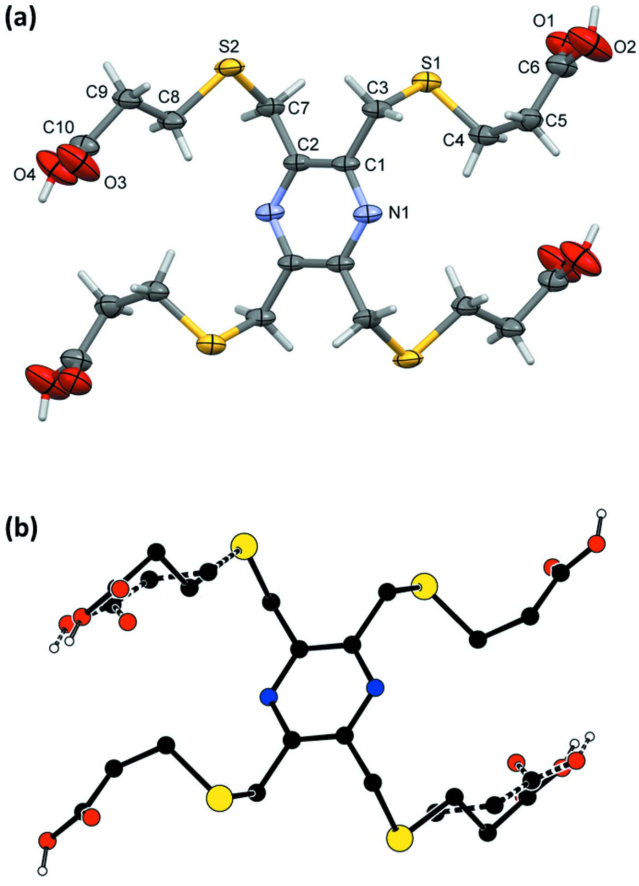


Figure 4
(*a*) The molecular structure of **H_4L1_B**, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level. (*b*) A view of the molecular structure of **H_4L1_B** with the symmetry-related disordered side chains (C8/C8*B*, C9/C9*B*, C10/C10*B*, O3/O3*B* and O4/O4*B*) shown with dashed bonds. Unlabelled atoms are related to labelled atoms by symmetry operator $-x + 2, -y + 1, -z + 1$.

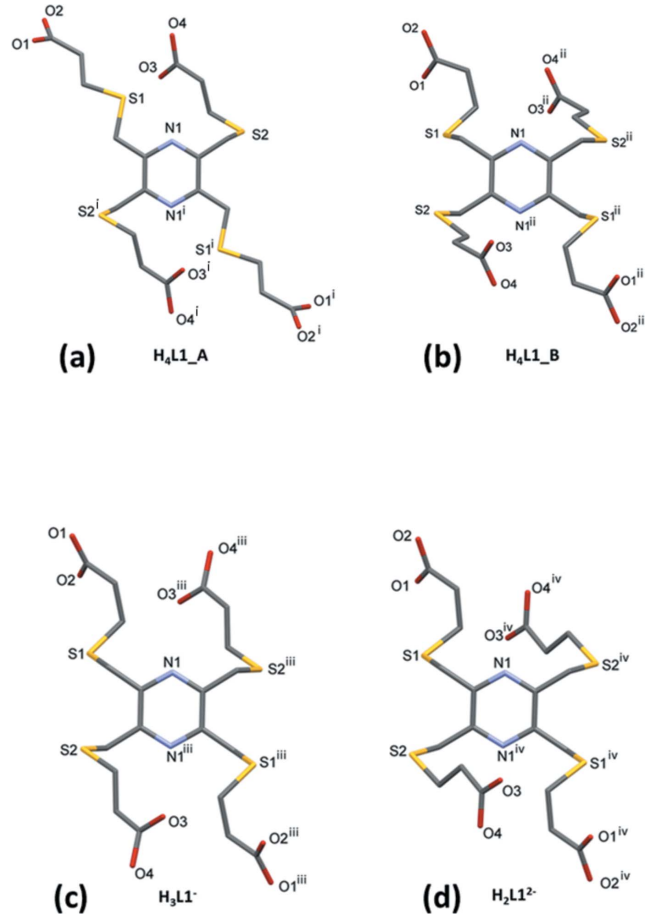


Figure 5
A comparison of the orientation of the $–CH_2—S—CH_2—CH_2–$ side chains in (*a*) polymorph **H_4L1_A**, (*b*) for the major disordered component of polymorph **H_4L1_B**, (*c*) **KH_3L1** and (*d*) **K_2H_2L1** [see Table 1 for further details; symmetry codes: (i) = (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $-x + \frac{1}{2}, -y + \frac{5}{2}, -z + 1$].

Table 2
Selected bond lengths (Å) for **KH$_3$L1**.

K1—O1	2.828 (2)	K1—O3^{ii}	2.682 (2)
K1—O2^{i}	3.056 (3)	K1—O4^{iii}	3.069 (3)

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

Table 3
Selected bond lengths (Å) for **K$_2$H$_2$L1**.

K1—O1^{i}	2.7084 (14)	K2—O1	2.7132 (13)
K1—O2	2.6682 (12)	K2—O3^{iii}	2.6682 (13)
K1—O3^{ii}	2.8099 (14)	K2—O4^{ii}	2.7209 (12)

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

Reaction of **H$_4$L1** with Hg(NO$_3$)$_2$ in the presence a 1 *M* potassium acetate buffer led to the formation of colourless crystals that proved to be a potassium–organic framework (**KH$_3$L1**); see Fig. 6. The asymmetric unit consists of half a mono-deprotonated ligand molecule located about an inversion center, and half a potassium ion located on an inversion center. The carboxy H atom is disordered by symmetry. The K$^+$ ion is linked to the O atoms of the acid groups and has a coordination number of eight (KO$_8$) and a distorted dodecahedral geometry (Fig. 7*a*). The K···O bond lengths vary between 2.682 (2) and 3.069 (3) Å (Table 2). Interestingly, here there is a significant difference between the K···O(C═O) and K···O(O$^-$) distances: 2.6823 (2) and 2.828 (2) Å compared to 3.056 (3) and 3.069 (3) Å, respectively.

Reaction of **H$_4$L1** with Zn(NO$_3$)$_2$ in the presence of a 1 *M* potassium acetate buffer led to the formation of colourless crystals that proved to be a dipotassium–organic framework (**K$_2$H$_2$L1**); see Fig. 8. The asymmetric unit consists of half a di-deprotonated ligand molecule located about an inversion center, and two half potassium ions located on inversion centers. The K$^+$ ions are linked to the O atoms of the acid

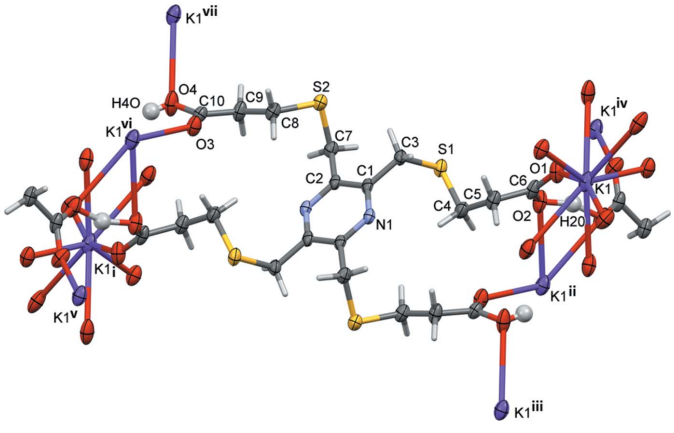


Figure 6
The molecular structure of complex **KH$_3$L1**, with labels for the atoms in the asymmetric unit of the organic anion. Unlabelled atoms are related to labelled atoms by symmetry operator (i) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$. Displacement ellipsoids are drawn at the 50% probability level. [Further symmetry codes are: (ii) $-x+1, -y, -z$: (iii) $x, y+1, z$; (iv) $x, y, z+1$; (v) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z-1$; (vi) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (vii) $-x+\frac{1}{2}, -y-\frac{1}{2}, -z$.]

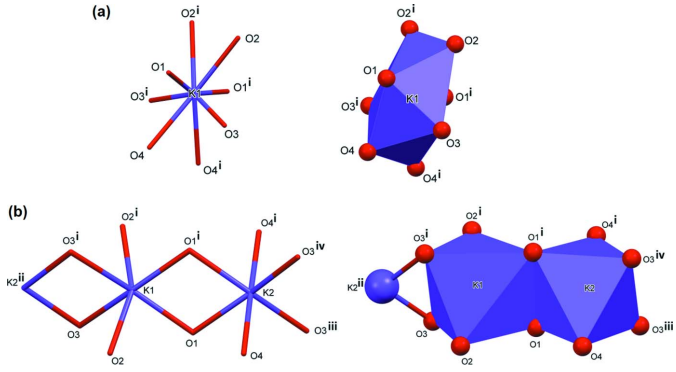


Figure 7
(*a*) Views of the coordination sphere of the potassium ion in **KH$_3$L1** [symmetry code: (i) $-x+1, y, -z-\frac{1}{2}$] and (*b*) views of the coordination sphere of the potassium ions in **K$_2$H$_2$L1** [symmetry codes: (i) $-x, y, -z+\frac{3}{2}$; (ii) $x, y-1, z$; (iii) $x, y+1, z$; (iv) $-x, y+1, -z+\frac{3}{2}$].

groups and both K$^+$ ions have a coordination number of six (KO$_6$) and have edge-sharing bipyramidal geometries. The K$^+$ ions are bridged by atoms O1 and O3, forming chains propagating along the *b*-axis direction (Fig. 7*b*). The K···O bond lengths vary between 2.6682 (12) and 2.8099 (14) Å (Table 3). Here, the difference between the K···O(C═O) and K···O(O$^-$) bond lengths is much less significant (Table 3).

The K···O bond lengths in the **KH$_3$L1** and **K$_2$H$_2$L1** frameworks are close to those observed for similar compounds; see §*6 Database survey*. The conformation of one of the –CH$_2$—S—CH$_2$—CH$_2$– side chains (involving atom S1) of the organic anion are similar, and similar to that in **H$_4$L1_B** (Fig. 5*b*), while the conformation of the second (involving atom S2) differs significantly (Fig. 5*c* and *d*, and Table 1).

3. Supramolecular features

In the crystal of **H$_4$L1_A**, molecules are linked by pairs of O—H···O hydrogen bonds, forming classical carboxylic acid

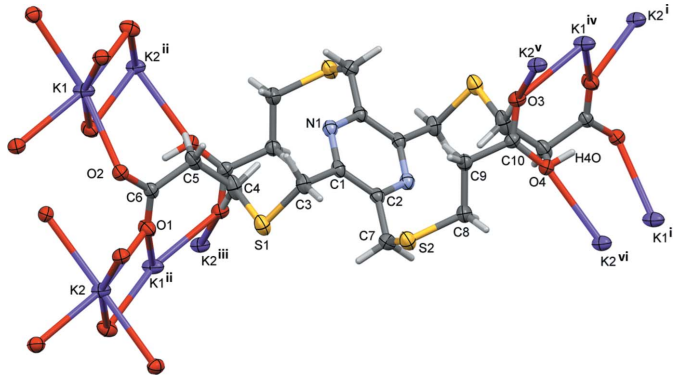


Figure 8
The molecular structure of complex **K$_2$H$_2$L1**, with labels for the atoms in the asymmetric unit of the organic dianion. Unlabelled atoms are related to labelled atoms by symmetry operator (i) $-x+\frac{1}{2}, -y+\frac{5}{2}, -z+1$. Displacement ellipsoids are drawn at the 50% probability level. [Further symmetry codes are: (ii) $-x, -y+2, -z+1$; (iii) $x, y+1, z$; (iv) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (v) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (vi) $x+\frac{1}{2}, y+\frac{1}{2}, z$.]

Table 4
Hydrogen-bond geometry (Å, °) for **H$_4$L1_A**.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1^{i}	0.87 (2)	1.80 (2)	2.667 (3)	172 (5)
O4—H4O···O3^{ii}	0.83 (2)	1.85 (2)	2.673 (3)	175 (5)
C5—H5A···O3^{iii}	0.97	2.55	3.405 (4)	147
C8—H8A···O4^{iv}	0.97	2.40	3.308 (4)	156

Symmetry codes: (i) $-x-1, -y, -z$; (ii) $-x+1, -y+1, -z$; (iii) $x-1, y, z$; (iv) $x+1, y, z$.

Table 5
Hydrogen-bond geometry (Å, °) for **H$_4$L1_B**.

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O3^{i}	0.82	1.94	2.66 (1)	146
O2—H2O···O3B^{i}	0.82	2.20	2.77 (3)	127
O4—H4O···O1^{ii}	0.82	1.88	2.66 (1)	158
O4B—H4OB···O1^{ii}	0.82	1.86	2.67 (4)	170

Symmetry codes: (i) $x, y, z+1$; (ii) $x, y, z-1$.

inversion dimers enclosing $R_2^2(8)$ loops (Fig. 9 and Table 4). These interactions lead to the formation of layers lying parallel to the *bc* plane. The layers are linked by C—H···O hydrogen bonds (Table 4), forming a supramolecular framework.

In the crystal of **H$_4$L1_B**, molecules are linked by pairs of O—H···O hydrogen bonds, forming chains propagating along the *c*-axis direction and enclosing $R_2^2(8)$ loops (Fig. 10 and Table 5). There are no other significant directional contacts present in the crystal.

In both **KH$_3$L1** and **K$_2$H$_2$L1**, the organic anions are arranged as rungs of parallel ladders, so forming the framework structures, as shown in Figs. 11 and 12, respectively. The frameworks are reinforced by O—H···O, C—H···O and C—H···N hydrogen bonds (Tables 6 and 7, respectively).

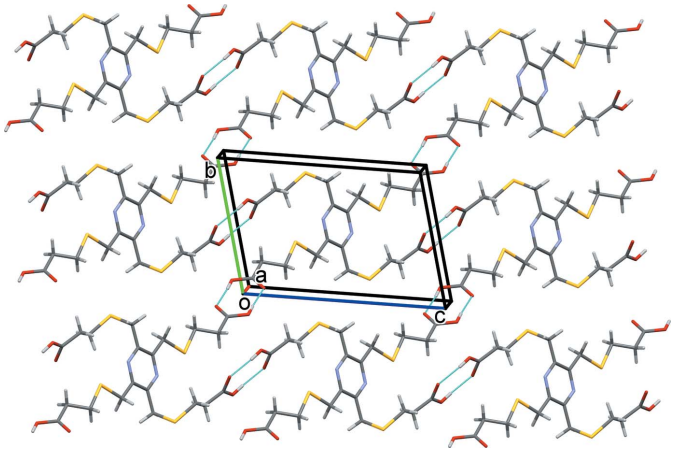


Figure 9
A view along the *a* axis of the crystal packing of **H$_4$L1_A**. The hydrogen bonds are shown as dashed lines (see Table 4).

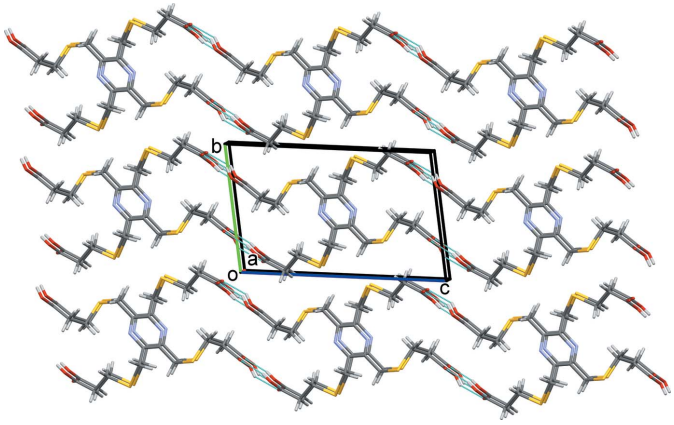


Figure 10
A view along the *a*-axis of the crystal packing of **H$_4$L1_B**. Only atoms of the major component are shown. The hydrogen bonds are shown as dashed lines (see Table 5).

Table 6
Hydrogen-bond geometry (Å, °) for **KH$_3$L1**.

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4O···O1^{iv}	0.80 (5)	1.86 (5)	2.661 (3)	180 (7)
O2—H20···O2^{v}	1.24 (1)	1.24 (1)	2.436 (3)	159 (7)
C4—H4A···N1	0.99	2.52	3.340 (4)	140
C4—H4B···O3^{vi}	0.99	2.49	3.114 (4)	121
C5—H5B···O2^{i}	0.99	2.60	3.467 (4)	146
C7—H7B···N1^{vii}	0.99	2.60	3.454 (4)	144
C9—H9A···O3^{vii}	0.99	2.58	3.465 (4)	149

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

Table 7
Hydrogen-bond geometry (Å, °) for **K$_2$H$_2$L1**.

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4O···O2^{iv}	0.85 (2)	1.61 (2)	2.4637 (16)	177 (3)
C4—H4A···N1	0.99	2.44	3.266 (2)	141
C8—H8A···O3^{v}	0.99	2.53	3.436 (2)	151

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

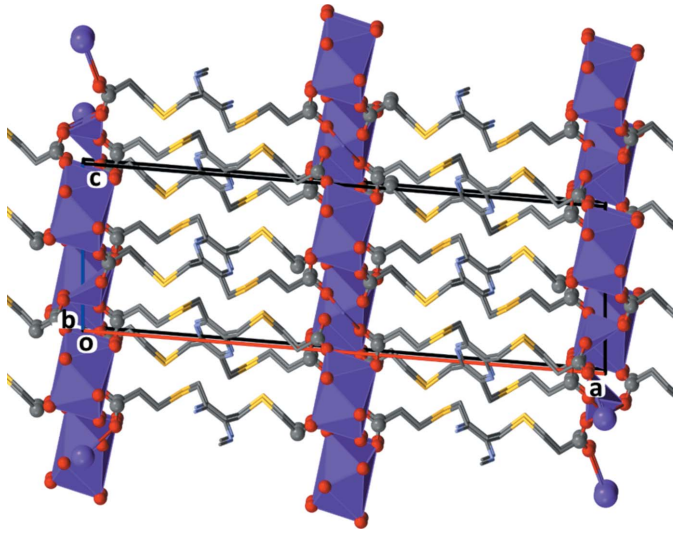


Figure 11
A view along the *b* axis of the crystal packing of complex **KH$_3$L1**. For clarity, the H atoms have been omitted.

Table 8
Short contacts (Å) in the crystal structures of **H$_4$L1_A** and **H$_4$L1_B**[a].

Atom 1	Atom 2	Length	Length − VdW	Symm. op. 1	Symm. op. 2
H$_4$L1_A					
O1	H2*O*	1.798	−0.922	*x*, *y*, *z*	−1 − *x*, −*y*, −*z*
O3	H4*O*	1.843	−0.877	*x*, *y*, *z*	1 − *x*, 1 − *y*, −*z*
O1	O2	2.667	−0.373	*x*, *y*, *z*	−1 − *x*, −*y*, −*z*
O3	O4	2.673	−0.367	*x*, *y*, *z*	1 − *x*, 1 − *y*, −*z*
O4	H8*A*	2.399	−0.321	*x*, *y*, *z*	−1 + *x*, *y*, *z*
O2	O4	3.015	−0.025	*x*, *y*, *z*	−*x*, 1 − *y*, −*z*
C6	H2*O*	2.667	−0.233	*x*, *y*, *z*	−1 − *x*, −*y*, −*z*
C10	H4*O*	2.668	−0.232	*x*, *y*, *z*	1 − *x*, 1 − *y*, −*z*
H5*A*	O3	2.549	−0.171	*x*, *y*, *z*	−1 + *x*, *y*, *z*
H4*O*	H4*O*	2.371	−0.029	*x*, *y*, *z*	1 − *x*, 1 − *y*, −*z*
H2*O*	H2*O*	2.389	−0.011	*x*, *y*, *z*	−1 − *x*, −*y*, −*z*
N1	H3*A*	2.807	0.057	*x*, *y*, *z*	1 − *x*, 1 − *y*, 1 − *z*
O4	C8	3.308	0.088	*x*, *y*, *z*	−1 + *x*, *y*, *z*
O2	H8*A*	2.820	0.100	*x*, *y*, *z*	1 − *x*, 1 − *y*, −*z*
H$_4$L1_B[a]					
H4*O*	O1	1.879	−0.841	*x*, *y*, *z*	*x*, *y*, −1 + *z*
O4	O1	2.658	−0.382	*x*, *y*, *z*	*x*, *y*, −1 + *z*
O3	O2	2.663	−0.377	*x*, *y*, *z*	*x*, *y*, −1 + *z*
H4*O*	C6	2.580	−0.320	*x*, *y*, *z*	*x*, *y*, −1 + *z*
O4	O2	2.799	−0.241	*x*, *y*, *z*	−1 + *x*, *y*, −1 + *z*
H4*O*	H2*O*	2.173	−0.227	*x*, *y*, *z*	*x*, *y*, −1 + *z*
O1	O2	2.982	−0.058	*x*, *y*, *z*	−1 + *x*, *y*, *z*
S1	H3*A*	2.951	−0.049	*x*, *y*, *z*	−1 + *x*, *y*, *z*
S1	S2	3.590	−0.010	*x*, *y*, *z*	1 − *x*, −*y*, 1 − *z*
O4	O3	3.041	0.001	*x*, *y*, *z*	−1 + *x*, *y*, *z*
S2	S2	3.613	0.013	*x*, *y*, *z*	1 − *x*, −*y*, 1 − *z*
H8*A*	O3	2.749	0.029	*x*, *y*, *z*	−1 + *x*, *y*, *z*
S1	H5*A*	3.047	0.047	*x*, *y*, *z*	−1 + *x*, *y*, *z*
H4*O*	O2	2.775	0.055	*x*, *y*, *z*	−1 + *x*, *y*, −1 + *z*
O4	H2*O*	2.776	0.056	*x*, *y*, *z*	−1 + *x*, *y*, −1 + *z*
C10	H2*O*	2.960	0.060	*x*, *y*, *z*	2 − *x*, −*y*, 1 − *z*
O3	H2*O*	2.796	0.076	*x*, *y*, *z*	2 − *x*, −*y*, 1 − *z*
H7*B*	C3	2.974	0.074	*x*, *y*, *z*	−1 + *x*, *y*, *z*
S2	H7*B*	3.082	0.082	*x*, *y*, *z*	1 − *x*, −*y*, 1 − *z*
O2	H5*B*	2.802	0.082	2 − *x*, 1 − *y*, 1 − *z*	−1 + *x*, *y*, −1 + *z*
S1	H9*A*	3.085	0.085	*x*, *y*, *z*	1 − *x*, −*y*, 1 − *z*

Note: (*a*) major component of **H$_4$L1_B**.

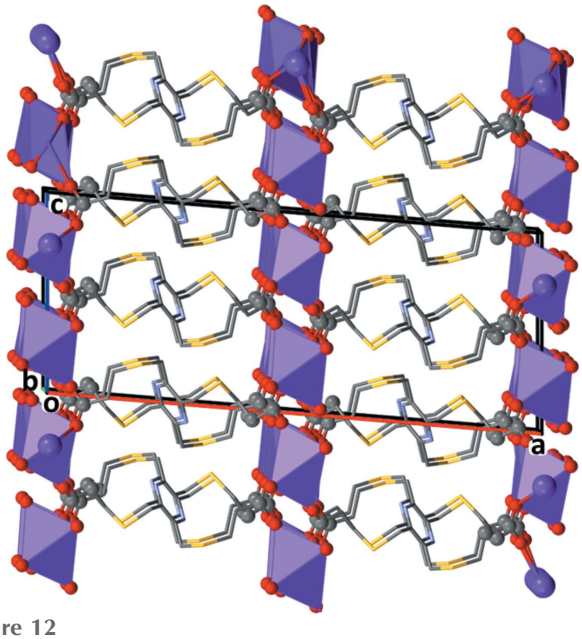


Figure 12
A view along the *b* axis of the crystal packing of complex **K$_2$H$_2$L1**. For clarity, the H atoms have been omitted.

4. Hirshfeld surface analysis and two-dimensional fingerprint plots for H$_4$L1_A, and H$_4$L1_B

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007) were performed with *CrystalExplorer17* (Turner *et al.*, 2017) following the protocol of Tiekink and collaborators (Tan *et al.*, 2019).

The Hirshfeld surfaces are colour-mapped with the normalized contact distance, d_{norm}, varying from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The Hirshfeld surfaces (HS) of **H$_4$L1_A**, and **H$_4$L1_B** mapped over d_{norm} are given in Fig. 13. The most significant short contacts in the crystal structures of the two polymorphs are given in Table 8. The large red spots in Fig. 13*a* and *b* concern the O—H···O hydrogen bonds in the crystal structures of both compounds.

The percentage contributions of inter-atomic contacts to the HS for both compounds are compared in Table 9. The two-dimensional fingerprint plots for compounds **H$_4$L1_A**, and **H$_4$L1_B** are shown in Fig. 14. They reveal that the principal

Table 9
Percentage contributions of inter-atomic contacts to the Hirshfeld surfaces of **H$_4$L1_A** and **H$_4$L1_B**[a].

Contact	% contribution	% contribution
	H$_4$L1_A	**H$_4$L1_B**[a]
H···H	37.2	36.3
O···H/H···O	37.7	32.2
S···H/H···S	13.4	16.1
C···H/H···C	4.5	4.9
N···H/H···N	3.0	2.5
C···N	0	0.8
C···O	1.0	0.7
C···S	1.2	0
N···S	0.4	0.4
O···O	1.3	4.9
O···S	0.2	0
S···S	0.2	1.2

Note: (*a*) major component of **H$_4$L1_B**.

contributions to the overall HS involve H···H contacts at 37.2 and 36.3%, respectively, and O···H/H···O contacts at, respectively, 37.7 and 32.2%.

The third most important contribution to the HS is from the S···H/H···S contacts at 13.4 and 16.1%, for **H$_4$L1_A**, and **H$_4$L1_B**, respectively. These are followed by C···H/H···H contacts at, respectively, 4.5 and 4.9%. The N···H/H···N contacts contribute, respectively, 3.0 and 2.5%.

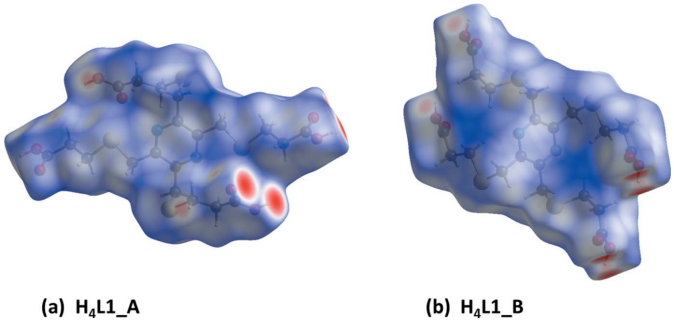


Figure 13
The Hirshfeld surfaces of compounds (*a*) **H$_4$L1_A** and (*b*) **H$_4$L1_B**, mapped over d_{norm} in the colour ranges of −0.7146 to 1.2167 and −0.6847 to 1.3548 au., respectively.

5. Energies frameworks for H$_4$L1_A, and H$_4$L1_B

The colour-coded interaction mappings within a radius of 6 Å of a central reference molecule for **H$_4$L1_A**, and **H$_4$L1_B**, are given in Fig. 15. Full details of the various contributions to the total energy (E_{tot}) are also included there; see Tan *et al.* (2019) for an explanation of the various parameters.

A comparison of the energy frameworks calculated for **H$_4$L1_A**, and **H$_4$L1_B**, showing the electrostatic potential forces (E_{ele}), the dispersion forces (E_{dis}) and the total energy diagrams (E_{tot}), are shown in Fig. 16. The energies were obtained by using the wave function at the HF/3-21G level of theory. The cylindrical radii are proportional to the relative strength of the corresponding energies (Turner *et al.*, 2017; Tan *et al.*, 2019). They have been adjusted to the same scale factor of 80 with a cut-off value of 5 kJ mol^{-1} within a radius of 6 Å of a central reference molecule. It can be seen that for both polymorphs the major contribution to the intermolecular interactions is from electrostatic potential forces (E_{ele}), reflecting the presence of the classical O—H···O hydrogen bonds.

6. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.42, last update February 2021; Groom *et al.*, 2016) for tetrakis-substituted pyrazine carboxylic acids gave results for only two such ligands, *viz*. 2,3,5,6-pyrazinetetracarboxylic acid (**pztca**) and 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (**pztba**). Ligand **pztba** has been shown to be extremely successful in forming metal–organic frameworks (Jiang *et al.*, 2017; Wang *et al.*, 2019).

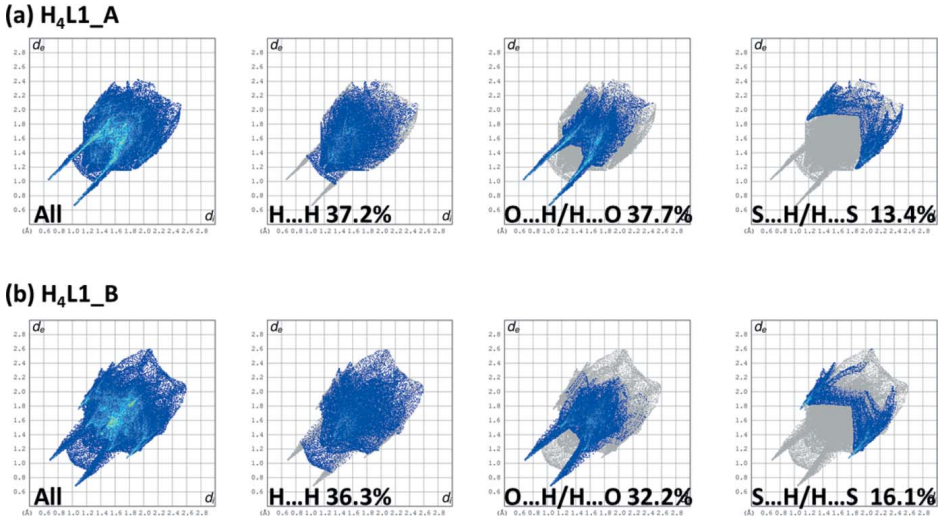
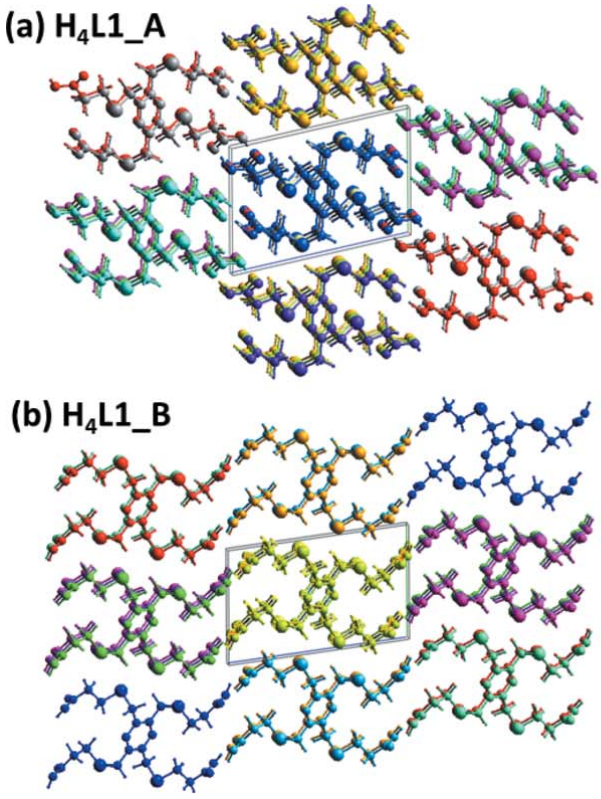


Figure 14
The full two-dimensional fingerprint plots for compounds (*a*) **H$_4$L1_A** and (*b*) **H$_4$L1_B**, and those delineated into H···H, O···H/H···O and S···H/H···S contacts.



	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	15.91	HF/3-21G	4.0	-1.6	-18.2	5.3	-9.1
	2	x, y, z	12.58	HF/3-21G	0.2	-0.8	-4.2	0.0	-4.2
	2	x, y, z	9.41	HF/3-21G	-10.9	-5.6	-38.2	21.6	-31.6
	2	x, y, z	13.52	HF/3-21G	-130.0	-43.8	-38.2	113.3	-103.4
	2	x, y, z	16.30	HF/3-21G	1.9	-1.8	-12.0	3.0	-7.7
	2	x, y, z	5.58	HF/3-21G	-70.5	-18.6	-125.2	72.9	-137.7
	2	x, y, z	9.01	HF/3-21G	-0.1	-1.3	-19.1	5.9	-13.4
	2	x, y, z	12.74	HF/3-21G	6.8	-1.2	-4.4	0.1	2.3

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	x, y, z	15.55	HF/3-21G	1.5	-0.2	-4.7	0.1	-2.8
	1	x, y, z	9.42	HF/3-21G	-30.0	-4.5	-36.4	40.7	-33.3
	1	x, y, z	4.94	HF/3-21G	-1.4	-14.1	-100.6	49.5	-61.1
	1	x, y, z	14.43	HF/3-21G	-13.5	-2.4	-18.6	10.0	-24.0
	1	x, y, z	15.85	HF/3-21G	-7.7	-1.4	-4.7	0.5	-12.6
	1	x, y, z	8.99	HF/3-21G	-4.2	-5.5	-46.7	20.6	-33.3
	0	x, y, z	17.70	HF/3-21G	5.7	-0.7	-1.3	0.0	4.1
	1	x, y, z	14.19	HF/3-21G	-188.9	-80.9	-40.4	188.2	-128.9
	0	x, y, z	15.60	HF/3-21G	1.8	-0.4	-1.6	0.0	0.2

Figure 15
The colour-coded interaction mappings within a radius of 6 Å of a central reference molecule for (*a*) **H$_4$L1_A** and (*b*) **H$_4$L1_B**.

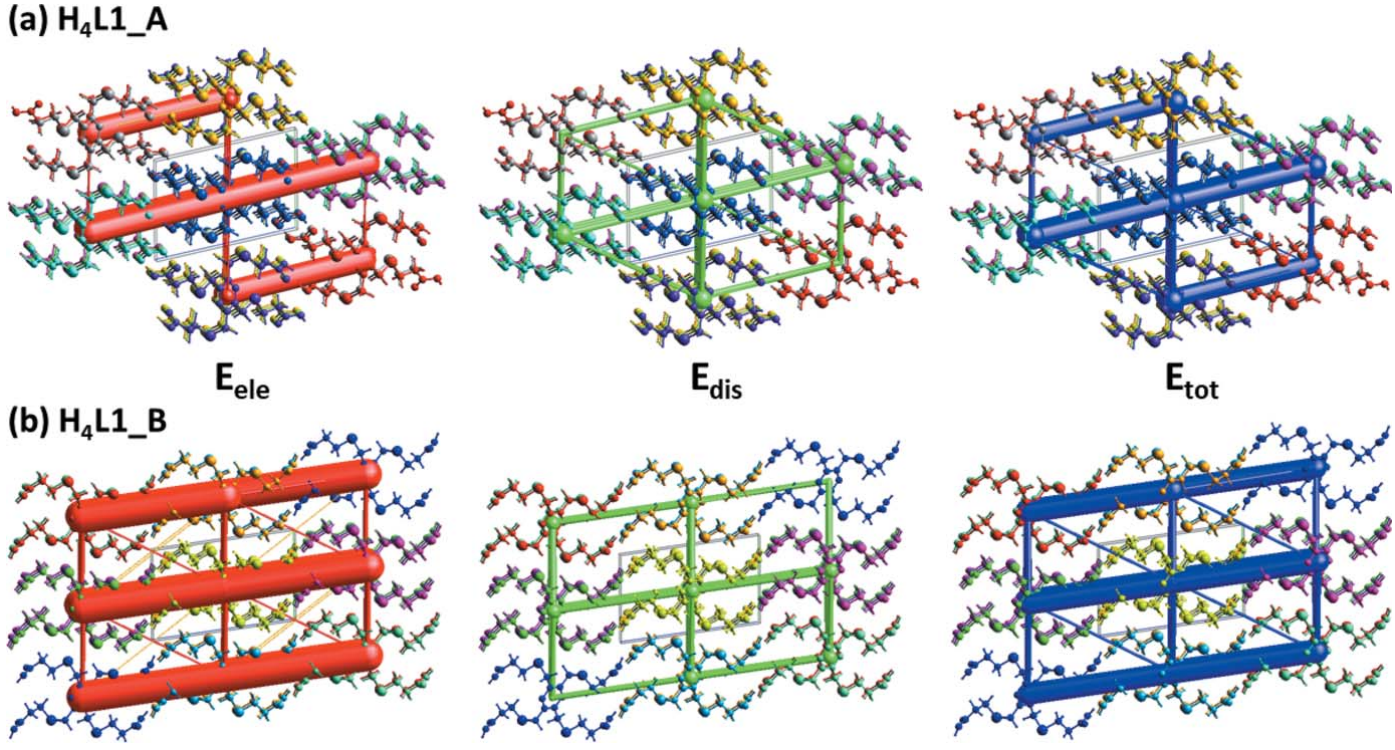


Figure 16
The energy frameworks calculated for (*a*) **H$_4$L1_A** and (*b*) **H$_4$L1_B**, both viewed along the *b*-axis direction, showing the electrostatic potential forces (E_{ele}), the dispersion forces (E_{dis}) and the total energy diagrams (E_{tot}).

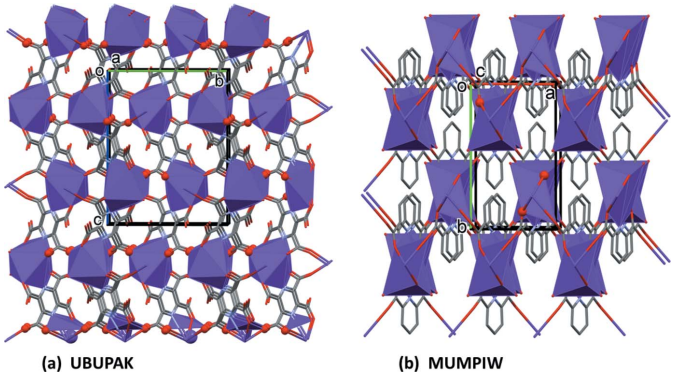


Figure 17
(*a*) A view along the *a* axis of the potassium–organic framework of UBUPAK (Masci *et al.*, 2010) and (*b*) a view along the *c* axis of the potassium–organic framework of MUMPIW (Li *et al.*, 2020).

Potassium salts of carboxylic acids are relatively common. A search for potassium salts of purely organic carboxylic acids and excluding hydrates, yielded over 200 hits. The potassium salt of **pztca** has been reported, *viz.* *catena*-[(μ_4-3,5,6-tricarboxypyrazine-2-carboxylato)potassium] (CSD refcode UBUPAK; Masci *et al.*, 2010). The structure of UBUPAK is that of a potassium–organic framework (Fig. 17*a*). The asymmetric unit consists of half a mono-deprotonated ligand molecule located about an inversion center, and half a potassium ion. The carboxy H atom is disordered by symmetry, similar to the situation in the structure of **KH$_3$L1**. Here the K···O bond lengths vary from 2.7951 (11) to 2.8668 (13) Å. The K$^+$ cation has a coordination number of 8 (KO_8) and a distorted dodecahedral geometry as in **KH$_3$L1** (Fig. 7*a* and 11).

The structure of the potassium salt of pyrazine-2,3-dicarboxylic acid (**pzdca**; Fig. 1), catena-[(μ_2-3-carboxypyrazine-2-carboxylato)-(μ_2-pyrazine-2,3-dicarboxylic acid)diaquapotassium], has been reported (RISYIC; Tombul *et al.*, 2008). It has a polymer chain structure with the chains linked by O—H···O hydrogen bonds, forming a supramolecular framework. Here the K···O bond lengths vary from 2.8772 (14) to 3.0898 (14) Å.

The structures of two potassium salts of 2,6-pyridine-dicarboxylic acid (**pydca**; Fig. 1) have been reported. They include, bis(μ_2-pyridine-2,6-dicarboxylic acid-*N,O,O′:O′*)-hexaaquabis(6-carboxypyridine-2-carboxylato-*O*)dipotassium (HAMBEE; Santra *et al.*, 2011; HAMBEE01; Hayati *et al.*, 2017), and *catena*-[(μ-6-carboxypyridine-2-carboxylato)-potassium] (MUMPIW; Li *et al.*, 2020). HAMBEE is a binuclear complex, which is linked by O—H···O hydrogen bonds to form supramolecular chains. The K···O bond lengths vary from 2.721 (2) to 3.054 (3) Å.

The structure of MUMPIW is that of a potassium-organic framework (Fig. 17*b*), with the K···O bonds lengths varying from 2.8197 (14) to 3.0449 (15) Å. The K$^+$ ion has a coordination number of seven (KO_6N) and has an edge-sharing pentagonal antiprism geometry, forming chains (Fig. 17*b*). This structure can be compared to that of **K$_2$H$_2$L1** where the two independent K$^+$ ions, each with a coordination number of six (KO_6), have edge-sharing bipyramidal geometries, also forming chains (Fig. 7*b* and 12).

7. Synthesis and crystallization

The synthesis and crystal structure of the reagent tetra-2,3,5,6-bromomethyl-pyrazine (TBr) have been reported (Ferigo *et al.*, 1994; Assoumatine & Stoeckli-Evans, 2014 [CSD refcode: TOJXUN]).

Synthesis of 3,3′,3″,3‴-{[pyrazine-2,3,5,6-tetrayltetrakis-(methylene)]tetrakis(sulfanediyl)}tetrapropionic acid (H$_4$L1):

Mercaptopropionic acid (1.8795 g, 1.77 mol, 4 eq) was dissolved in 50 ml THF. A minimum amount of water (a few ml) was added to dissolve 1.4166 g (3.54 mol, 8 eq) of NaOH. The volume of the mixture was increased to 100 ml by adding THF and the reaction was stirred under reflux for 1 h. Then TBr (2 g, 4.42 mol, 1 eq) dissolved in 50 ml THF was added dropwise using an addition funnel. The mixture was stirred under reflux for 6 h. After drying under vacuum, the residue was dissolved in 50 ml of deionized water, and HCl puriss. was added dropwise until a clearly acid pH was obtained. This mixture was stirred at room temperature for 1–2 h. The yellow precipitate that formed was filtered off and washed with a minimum amount of water and then $CHCl_3$. It was then dried under vacuum conditions. Recrystallization carried out with methanol gave pale-yellow crystals of **H$_4$L1** (yield 88%, m.p. 466 K) that X-ray diffraction analysis indicated to be triclinic polymorph **H$_4$L1_A**.

The presence of terephthalic acid in an equimolar quantity with **H$_4$L1** in methanol gave colourless crystals of rather poor quality. However, X-ray diffraction analysis indicated that a second triclinic ($P\bar{1}$) polymorph, **H$_4$L1_B**, had been obtained.

Spectroscopic and elemental analyses:

R_f: 0.77 (solvent: CH_3OH).

^{1}H NMR (CD_3OD, 400 MHz), δ(ppm): 4.03 (*s*, 8H, H2), 2.78 (*t*, 8H, $^3J_{(3,4)}$ = 7.0, H3), 2.62 (*t*, 8H, $^3J_{(4,3)}$ = 7.0, H4).

^{13}C NMR (CD_3OD, 50 MHz), δ(ppm): 174.54 (4C, C5), 150.12 (4C, C1), 34.29 (4C, C4), 33.64 (4C, C2), 26.65 (4C, C3).

Elemental Analysis for $C_{20}H_{28}N_2O_8S_4$, M_w = 552.71 g mol^{-1}: Calculated: C 43.46, H 5.11, N 5.07%. Found: C 43.40, H 5.17, N 4.87%.

ESI–MS, *m*/*z*: 591.04 [*M* + K]$^+$; 575.06 [*M* + Na]$^+$; 553.08 [*M* + H]$^+$; 471.07; 449.09.

IR (KBr disc, cm^{-1}) *ν*: 2926(*s*), 2666(*m*), 2590(*s*), 1693(*s*), 1429(*s*), 1406(*s*), 1340(*m*), 1270(s), 1200(*s*), 1163(*m*), 1134(*s*), 1107(*m*), 1055(*w*), 918(*s*), 658(*m*), 489(*m*).

Synthesis of poly[(μ-3-{[(3,5,6-tris{[(2-carboxyethyl)sulfanyl]methyl}pyrazin-2-yl)methyl]sulfanyl}propanoate)potassium] (KH$_3$L1):

Hg(NO$_3$)$_2$ (45.0 mg, 0.109 mmol, 2 eq) and **H$_4$L1** (30 mg, 0.054 mmol, 1 eq) were mixed together in 20 ml of a 1 *M* potassium acetate buffer. The mixture was left at 323 K under stirring and nitrogen conditions for 1 h. The mixture was then filtered and left to evaporate in air for six weeks. Colourless plate-like crystals were obtained, which were shown to be a potassium–organic framework.

Table 10
Experimental details.

	H_4L1_A	**H_4L1_B**	**KH_3L1**	**K_2H_2L1**
Crystal data				
Chemical formula	$C_{20}H_{28}N_2O_8S_4$	$C_{20}H_{28}N_2O_8S_4$	$[K(C_{20}H_{27}N_2O_8S_4)]$	$[K_2(C_{20}H_{26}N_2O_8S_4)]$
M_r	552.68	552.68	590.77	628.87
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
Temperature (K)	293	293	153	153
a, b, c (Å)	5.5843 (8), 9.0061 (14), 12.739 (2)	4.9424 (17), 8.993 (3), 14.190 (6)	30.080 (4), 8.4716 (10), 9.5908 (12)	27.908 (2), 8.2916 (6), 11.3035 (9)
α, β, γ (°)	101.537 (18), 94.313 (18), 103.701 (17)	96.96 (3), 97.14 (3), 100.72 (3)	90, 94.717 (11), 90	90, 94.753 (6), 90
V (Å^3)	604.80 (17)	608.1 (4)	2435.7 (6)	2606.7 (3)
Z	1	1	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.44	0.44	0.61	0.73
Crystal size (mm)	0.35 × 0.30 × 0.05	0.50 × 0.50 × 0.05	0.50 × 0.50 × 0.10	0.50 × 0.50 × 0.05
Data collection				
Diffractometer	Stoe IPDS 1	Stoe IPDS 2	Stoe IPDS 2	Stoe IPDS 2
Absorption correction	Empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)	Empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)	Multi-scan (*MULABS*; Spek, 2020)	Empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)
T_{min}, T_{max}	0.647, 0.897	0.144, 0.616	0.640, 1.000	0.416, 0.803
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4709, 2194, 1452	4152, 2201, 1537	10309, 2084, 1646	19423, 3646, 3175
R_{int}	0.058	0.080	0.064	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.615	0.617	0.590	0.695
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.097, 0.88	0.071, 0.208, 1.05	0.039, 0.106, 1.02	0.037, 0.103, 1.05
No. of reflections	2194	2201	2084	3646
No. of parameters	162	173	165	167
No. of restraints	2	6	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.28	0.47, −0.39	0.26, −0.36	0.76, −0.51

Computer programs: *EXPOSE*, *CELL* and *INTEGRATE* in *IPDS*-I (Stoe & Cie, 2000), *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015), *PLATON* (Spek, 2020) *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

IR (KBr disc, cm^{-1}) ν: 3422(*m*), 2922(*m*), 1713(*m*), 1580(*s*), 1399(*s*), 1247(*m*), 1190(*m*), 1152(*m*), 1114(*m*), 811(*m*), 787(*m*).

Synthesis of poly[(μ-3,3′-{[(3,6-bis{[(2-carboxyethyl)sulfanyl]methyl}pyrazine-2,5-diyl)bis(methylene)]bis(sulfanediyl)}dipropionato)dipotassium] (K_2H_2L1):

$Zn(NO_3)_2$ (28.4 mg, 0.109 mmol, 2 eq) and **H_4L1** (30 mg, 0.054 mmol, 1eq) were mixed together in 20 ml of a 1M potassium acetate buffer. The mixture was left at 323 K under stirring and nitrogen for 1 h. The mixture was then filtered and left to evaporate in air for 6 weeks. Colourless plate-like crystals were obtained, which proved to be a dipotassium-organic framework.

IR (KBr disc, cm^{-1}) ν: 3401(*m*), 1579(*s*), 1401(*s*), 1303(*m*).

8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 10.

For **H_4L1_A**, **KH_3L1** and **K_2H_2L1**, the various –CO_2H H atoms were located in difference-Fourier maps and freely refined. For **H_4L1_B**, the –CO_2H H atoms were difficult to locate, probably due to the poor quality of the crystal and the disorder in the side chain (atoms C8/C8*B*, C9/C9*B*, C10/C10*B*, O3/O3*B*, O4/O4*B*; Fig. 4*b*). They were therefore included in calculated positions assuming the formation of carboxylic acid dimers; O—H = 0.82 Å and refined as riding with U_{iso}(H) = 1.5U_{eq}(O).

As in the K^+ salt of pyrazine tetracarboxylic acid (UBUPAK; Masci *et al.*, 2010), the carboxy H atom in **KH_3L1** is disordered by symmetry, hence the H atom on O3 was given an occupancy factor of 0.5 to balance the charges.

For all four compounds, the C-bound H atoms were included in calculated positions and treated as riding on their parent C atom with C—H = 0.97 Å and U_{iso}(H) = 1.2U_{eq}(C).

For **H_4L1_A** and **H_4L1_B**, the alert _diffrn_reflns_point_group_measured_fraction_full value (0.94 and 0.93, respectively) below minimum (0.95) was given. For **H_4L1_A** it involves 131 random reflections out of a total of 2180, *viz.* 6.0%, while for **H_4L1_B** it involves 158 random reflections out of a total of 2184, *viz.* 7.2%.

For **H_4L1_A**, **H_4L1_B** and **K_2H_2L1** the multiplicity of reflections was 2 or less and so an empirical absorption correction was applied.

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supporting information

Acta Cryst. (2021). E**77**, 480-490 [https://doi.org/10.1107/S2056989021003479]

A new tetrakis-substituted pyrazine carboxylic acid, 3,3′,3″,3‴-{[pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis-(sulfanediyl)}tetrapropionic acid: crystal structures of two triclinic polymorphs and of two potassium–organic frameworks

Jessica Pacifico and Helen Stoeckli-Evans

Computing details

Data collection: *EXPOSE* in *IPDS*-I (Stoe & Cie, 2000) for H4L1A; *X-AREA* (Stoe & Cie, 2002) for H4L1B, KH3L1, K2H2L1. Cell refinement: *CELL* in *IPDS*-I (Stoe & Cie, 2000) for H4L1A; *X-AREA* (Stoe & Cie, 2002) for H4L1B, KH3L1, K2H2L1. Data reduction: *INTEGRATE* in *IPDS*-I (Stoe & Cie, 2000) for H4L1A; *X-RED32* (Stoe & Cie, 2002) for H4L1B, KH3L1, K2H2L1. For all structures, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2015). Molecular graphics: *Mercury* (Macrae *et al.*, 2020) for H4L1A; *PLATON* (Spek, 2020) and *Mercury* (Macrae *et al.*, 2020) for H4L1B, KH3L1, K2H2L1. For all structures, software used to prepare material for publication: *SHELXL2018*/3 (Sheldrick, 2015), *PLATON* (Spek, 2020) and *publCIF* (Westrip, 2010).

3,3′,3″,3‴-{[Pyrazine-2,3,5,6-tetrayltetrakis(methylene)]tetrakis(sulfanediyl]}tetrapropionic acid (H4L1A)

Crystal data

$C_{20}H_{28}N_2O_8S_4$
M_r = 552.68
Triclinic, $P\overline{1}$
a = 5.5843 (8) Å
b = 9.0061 (14) Å
c = 12.739 (2) Å
α = 101.537 (18)°
β = 94.313 (18)°
γ = 103.701 (17)°
V = 604.80 (17) Å^3
Z = 1
$F(000)$ = 290
D_x = 1.517 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3225 reflections
θ = 2.4–25.9°
μ = 0.44 mm^{-1}
T = 293 K
Plate, pale-yellow
0.35 × 0.30 × 0.05 mm

Data collection

STOE IPDS 1 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
φ rotation scans
Absorption correction: empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)
T_{min} = 0.647, T_{max} = 0.897
4709 measured reflections
2194 independent reflections
1452 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 25.9°, θ_{min} = 2.4°
h = −6→6
k = −11→11
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.097$
$S = 0.88$
2194 reflections
162 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.40170 (15)	0.39121 (9)	0.29698 (6)	0.0312 (2)
S2	1.27548 (15)	0.86290 (9)	0.37908 (6)	0.0288 (2)
O1	−0.3381 (5)	0.0716 (3)	0.12207 (17)	0.0435 (6)
O2	−0.2098 (5)	0.1064 (3)	−0.03567 (17)	0.0409 (6)
H2O	−0.363 (5)	0.052 (5)	−0.059 (4)	0.098 (19)*
O3	0.7761 (4)	0.5277 (3)	0.08084 (16)	0.0379 (6)
O4	0.5045 (5)	0.6736 (3)	0.09232 (19)	0.0422 (6)
H4O	0.422 (8)	0.607 (4)	0.039 (3)	0.087 (17)*
N1	0.8353 (4)	0.5540 (3)	0.44074 (17)	0.0198 (5)
C1	0.7859 (5)	0.4024 (3)	0.4451 (2)	0.0194 (6)
C2	1.0447 (5)	0.6523 (3)	0.4952 (2)	0.0183 (6)
C3	0.5460 (5)	0.2957 (3)	0.3850 (2)	0.0248 (6)
H3A	0.434405	0.264980	0.436177	0.030*
H3B	0.577409	0.201607	0.342827	0.030*
C4	0.1473 (6)	0.2234 (4)	0.2308 (2)	0.0328 (7)
H4A	0.202811	0.128008	0.222673	0.039*
H4B	0.011542	0.214305	0.274306	0.039*
C5	0.0600 (6)	0.2449 (4)	0.1219 (2)	0.0347 (8)
H5A	0.041788	0.350865	0.129466	0.042*
H5B	0.186183	0.233148	0.074799	0.042*
C6	−0.1807 (6)	0.1321 (3)	0.0698 (2)	0.0291 (7)
C7	1.0877 (6)	0.8196 (3)	0.4857 (2)	0.0239 (6)
H7A	1.170302	0.887935	0.554088	0.029*
H7B	0.928434	0.841937	0.471163	0.029*
C8	1.0935 (6)	0.7220 (4)	0.2615 (2)	0.0277 (7)
H8A	1.187763	0.725553	0.200717	0.033*
H8B	1.068152	0.617707	0.275367	0.033*
C9	0.8427 (6)	0.7491 (3)	0.2307 (2)	0.0290 (7)

H9A	0.742172	0.735720	0.288698	0.035*
H9B	0.866452	0.856524	0.223186	0.035*
C10	0.7046 (6)	0.6407 (4)	0.1277 (2)	0.0283 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0292 (5)	0.0246 (4)	0.0348 (4)	−0.0018 (3)	−0.0101 (3)	0.0109 (3)
S2	0.0243 (5)	0.0241 (4)	0.0376 (4)	−0.0013 (3)	0.0027 (3)	0.0156 (3)
O1	0.0333 (15)	0.0501 (14)	0.0362 (13)	−0.0022 (12)	−0.0093 (10)	0.0054 (11)
O2	0.0322 (16)	0.0486 (14)	0.0345 (13)	0.0001 (13)	−0.0099 (10)	0.0099 (10)
O3	0.0400 (15)	0.0425 (13)	0.0341 (12)	0.0216 (12)	−0.0002 (10)	0.0039 (10)
O4	0.0345 (15)	0.0519 (15)	0.0396 (13)	0.0217 (13)	−0.0064 (11)	0.0004 (12)
N1	0.0182 (14)	0.0159 (11)	0.0242 (11)	0.0010 (10)	−0.0009 (9)	0.0072 (9)
C1	0.0184 (16)	0.0158 (13)	0.0222 (13)	0.0006 (12)	0.0005 (10)	0.0055 (10)
C2	0.0182 (16)	0.0125 (12)	0.0226 (13)	0.0011 (12)	0.0009 (10)	0.0047 (10)
C3	0.0191 (17)	0.0189 (14)	0.0327 (15)	−0.0025 (13)	−0.0028 (11)	0.0085 (11)
C4	0.0259 (19)	0.0290 (16)	0.0359 (16)	−0.0069 (14)	−0.0053 (13)	0.0097 (13)
C5	0.032 (2)	0.0279 (16)	0.0404 (18)	0.0008 (15)	−0.0080 (14)	0.0114 (13)
C6	0.0228 (19)	0.0264 (16)	0.0360 (17)	0.0048 (15)	−0.0074 (13)	0.0083 (13)
C7	0.0251 (18)	0.0155 (13)	0.0313 (15)	0.0028 (13)	0.0021 (12)	0.0088 (11)
C8	0.0263 (18)	0.0316 (16)	0.0293 (15)	0.0092 (14)	0.0066 (12)	0.0132 (12)
C9	0.0281 (19)	0.0276 (16)	0.0324 (16)	0.0074 (15)	0.0008 (12)	0.0097 (12)
C10	0.0262 (18)	0.0385 (17)	0.0254 (15)	0.0125 (15)	0.0068 (12)	0.0129 (13)

Geometric parameters (Å, º)

S1—C3	1.796 (3)	C3—H3B	0.9700
S1—C4	1.818 (3)	C4—C5	1.500 (4)
S2—C8	1.813 (3)	C4—H4A	0.9700
S2—C7	1.825 (3)	C4—H4B	0.9700
O1—C6	1.233 (4)	C5—C6	1.493 (4)
O2—C6	1.307 (4)	C5—H5A	0.9700
O2—H2O	0.87 (2)	C5—H5B	0.9700
O3—C10	1.240 (4)	C7—H7A	0.9700
O4—C10	1.294 (4)	C7—H7B	0.9700
O4—H4O	0.830 (19)	C8—C9	1.514 (4)
N1—C2	1.332 (3)	C8—H8A	0.9700
N1—C1	1.341 (3)	C8—H8B	0.9700
C1—C2^{i}	1.406 (3)	C9—C10	1.499 (4)
C1—C3	1.499 (4)	C9—H9A	0.9700
C2—C7	1.500 (3)	C9—H9B	0.9700
C3—H3A	0.9700		
C3—S1—C4	97.53 (13)	C4—C5—H5B	108.8
C8—S2—C7	101.68 (14)	H5A—C5—H5B	107.7
C6—O2—H2O	108 (3)	O1—C6—O2	123.6 (3)
C10—O4—H4O	113 (3)	O1—C6—C5	122.7 (3)

C2—N1—C1	119.1 (2)	O2—C6—C5	113.7 (3)
N1—C1—C2^{i}	120.3 (2)	C2—C7—S2	112.8 (2)
N1—C1—C3	117.7 (2)	C2—C7—H7A	109.0
C2^{i}—C1—C3	122.0 (2)	S2—C7—H7A	109.0
N1—C2—C1^{i}	120.6 (2)	C2—C7—H7B	109.0
N1—C2—C7	115.9 (2)	S2—C7—H7B	109.0
C1^{i}—C2—C7	123.4 (2)	H7A—C7—H7B	107.8
C1—C3—S1	110.88 (18)	C9—C8—S2	114.2 (2)
C1—C3—H3A	109.5	C9—C8—H8A	108.7
S1—C3—H3A	109.5	S2—C8—H8A	108.7
C1—C3—H3B	109.5	C9—C8—H8B	108.7
S1—C3—H3B	109.5	S2—C8—H8B	108.7
H3A—C3—H3B	108.1	H8A—C8—H8B	107.6
C5—C4—S1	109.2 (2)	C10—C9—C8	113.5 (2)
C5—C4—H4A	109.8	C10—C9—H9A	108.9
S1—C4—H4A	109.8	C8—C9—H9A	108.9
C5—C4—H4B	109.8	C10—C9—H9B	108.9
S1—C4—H4B	109.8	C8—C9—H9B	108.9
H4A—C4—H4B	108.3	H9A—C9—H9B	107.7
C6—C5—C4	113.8 (3)	O3—C10—O4	122.8 (3)
C6—C5—H5A	108.8	O3—C10—C9	122.4 (3)
C4—C5—H5A	108.8	O4—C10—C9	114.8 (3)
C6—C5—H5B	108.8		

C2—N1—C1—C2^{i}	−1.2 (4)	C4—C5—C6—O1	26.8 (4)
C2—N1—C1—C3	178.6 (2)	C4—C5—C6—O2	−154.4 (3)
C1—N1—C2—C1^{i}	1.2 (4)	N1—C2—C7—S2	−94.0 (3)
C1—N1—C2—C7	179.6 (2)	C1^{i}—C2—C7—S2	84.3 (3)
N1—C1—C3—S1	11.3 (3)	C8—S2—C7—C2	57.6 (2)
C2^{i}—C1—C3—S1	−168.8 (2)	C7—S2—C8—C9	65.7 (2)
C4—S1—C3—C1	174.1 (2)	S2—C8—C9—C10	174.8 (2)
C3—S1—C4—C5	−155.3 (2)	C8—C9—C10—O3	8.8 (4)
S1—C4—C5—C6	−167.9 (2)	C8—C9—C10—O4	−171.8 (3)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O1^{ii}	0.87 (2)	1.80 (2)	2.667 (3)	172 (5)
O4—H4*O*···O3^{iii}	0.83 (2)	1.85 (2)	2.673 (3)	175 (5)
C5—H5*A*···O3^{iv}	0.97	2.55	3.405 (4)	147
C8—H8*A*···O4^{v}	0.97	2.40	3.308 (4)	156

Symmetry codes: (ii) −*x*−1, −*y*, −*z*; (iii) −*x*+1, −*y*+1, −*z*; (iv) *x*−1, *y*, *z*; (v) *x*+1, *y*, *z*.

3,3′,3″,3‴-{[Pyrazine-2,3,5,6-tetrayltetrakis(methylene))tetrakis(sulfanediyl]}tetrapropionic acid (H4L1B)

Crystal data

$C_{20}H_{28}N_2O_8S_4$
M_r = 552.68
Triclinic, $P\overline{1}$
a = 4.9424 (17) Å
b = 8.993 (3) Å
c = 14.190 (6) Å
α = 96.96 (3)°
β = 97.14 (3)°
γ = 100.72 (3)°
V = 608.1 (4) Å^3
Z = 1
$F(000)$ = 290
D_x = 1.509 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5563 reflections
θ = 2.4–25.5°
μ = 0.44 mm^{-1}
T = 293 K
Plate, colourless
0.50 × 0.50 × 0.05 mm

Data collection

STOE IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
$\varphi + \omega$ scans
Absorption correction: empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)
T_{min} = 0.144, T_{max} = 0.616
4152 measured reflections
2201 independent reflections
1537 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
θ_{max} = 26.0°, θ_{min} = 2.3°
h = −5→5
k = −11→9
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.071
$wR(F^2)$ = 0.208
S = 1.05
2201 reflections
173 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1049P)^2 + 0.4241P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
S1	0.7886 (3)	0.28919 (12)	0.71512 (9)	0.0583 (4)	
S2	0.6227 (3)	0.07568 (12)	0.39724 (10)	0.0682 (5)	
N1	1.2114 (8)	0.5110 (4)	0.5754 (3)	0.0500 (9)	
C1	0.9965 (9)	0.3908 (4)	0.5566 (3)	0.0467 (10)	
C2	0.7852 (9)	0.3796 (4)	0.4821 (3)	0.0469 (10)	
C3	1.0020 (10)	0.2707 (4)	0.6214 (3)	0.0537 (11)	
H3A	1.192760	0.277226	0.650755	0.064*	

H3B	0.937959	0.170470	0.583113	0.064*	
C4	0.9971 (12)	0.4560 (5)	0.7916 (4)	0.0644 (13)	
H4A	1.087916	0.524956	0.752231	0.077*	
H4B	0.876729	0.509027	0.826037	0.077*	
C5	1.2177 (12)	0.4158 (6)	0.8638 (4)	0.0682 (14)	
H5A	1.332589	0.358948	0.829232	0.082*	
H5B	1.337009	0.509683	0.898069	0.082*	
C6	1.0984 (14)	0.3238 (6)	0.9345 (4)	0.0728 (15)	
O1	0.8532 (10)	0.3158 (5)	0.9473 (3)	0.0828 (12)	
O2	1.2630 (12)	0.2603 (9)	0.9826 (5)	0.136 (2)	
H2O	1.173990	0.186783	1.001978	0.204*	
C7	0.5410 (10)	0.2468 (5)	0.4572 (4)	0.0559 (11)	
H7A	0.394220	0.276430	0.416093	0.067*	
H7B	0.470023	0.224151	0.515671	0.067*	
C8	0.6926 (16)	0.1494 (6)	0.2872 (5)	0.0604 (17)	0.821 (6)
H8A	0.530565	0.183752	0.258819	0.072*	0.821 (6)
H8B	0.847467	0.236521	0.301719	0.072*	0.821 (6)
C9	0.7607 (15)	0.0292 (6)	0.2173 (5)	0.0657 (16)	0.821 (6)
H9A	0.597449	−0.051856	0.196091	0.079*	0.821 (6)
H9B	0.906849	−0.014697	0.248293	0.079*	0.821 (6)
C10	0.8546 (16)	0.0963 (7)	0.1325 (5)	0.0622 (15)	0.821 (6)
O3	1.0881 (16)	0.0900 (11)	0.1127 (6)	0.132 (3)	0.821 (6)
O4	0.6974 (19)	0.1598 (10)	0.0858 (6)	0.117 (3)	0.821 (6)
H4O	0.785351	0.212989	0.052298	0.175*	0.821 (6)
C8B	0.834 (7)	0.112 (3)	0.3062 (18)	0.0604 (17)	0.179 (6)
H8B1	0.957385	0.212176	0.321614	0.072*	0.179 (6)
H8B2	0.941870	0.034250	0.294752	0.072*	0.179 (6)
C9B	0.609 (6)	0.106 (3)	0.2219 (19)	0.0657 (16)	0.179 (6)
H9B1	0.490282	0.005115	0.207464	0.079*	0.179 (6)
H9B2	0.494650	0.179949	0.237286	0.079*	0.179 (6)
C10B	0.748 (6)	0.143 (4)	0.137 (2)	0.0622 (15)	0.179 (6)
O3B	0.998 (6)	0.188 (6)	0.137 (3)	0.132 (3)	0.179 (6)
O4B	0.576 (9)	0.176 (6)	0.073 (3)	0.117 (3)	0.179 (6)
H4OB	0.660348	0.228397	0.038152	0.175*	0.179 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0546 (9)	0.0462 (6)	0.0762 (8)	0.0041 (5)	0.0158 (6)	0.0205 (5)
S2	0.0868 (11)	0.0329 (5)	0.0834 (9)	−0.0047 (5)	0.0293 (7)	0.0119 (5)
N1	0.045 (2)	0.0322 (16)	0.075 (2)	0.0074 (14)	0.0141 (17)	0.0146 (15)
C1	0.048 (3)	0.0259 (16)	0.071 (3)	0.0081 (15)	0.017 (2)	0.0160 (16)
C2	0.045 (3)	0.0292 (17)	0.070 (3)	0.0054 (15)	0.017 (2)	0.0152 (16)
C3	0.051 (3)	0.0350 (19)	0.080 (3)	0.0097 (17)	0.015 (2)	0.0220 (19)
C4	0.073 (4)	0.043 (2)	0.083 (3)	0.009 (2)	0.026 (3)	0.022 (2)
C5	0.063 (4)	0.061 (3)	0.077 (3)	−0.001 (2)	0.015 (3)	0.017 (2)
C6	0.064 (4)	0.066 (3)	0.090 (4)	0.003 (2)	0.013 (3)	0.033 (3)
O1	0.079 (3)	0.086 (3)	0.093 (3)	0.019 (2)	0.029 (2)	0.034 (2)

O2	0.085 (4)	0.190 (6)	0.162 (5)	0.031 (4)	0.031 (3)	0.122 (5)
C7	0.051 (3)	0.042 (2)	0.073 (3)	−0.0032 (18)	0.012 (2)	0.0155 (19)
C8	0.078 (5)	0.034 (3)	0.074 (4)	0.010 (2)	0.023 (3)	0.017 (2)
C9	0.084 (5)	0.040 (3)	0.079 (4)	0.011 (3)	0.026 (3)	0.022 (3)
C10	0.068 (5)	0.048 (3)	0.080 (4)	0.019 (3)	0.024 (3)	0.020 (3)
O3	0.096 (5)	0.194 (8)	0.145 (6)	0.052 (5)	0.052 (4)	0.113 (6)
O4	0.132 (8)	0.140 (5)	0.131 (5)	0.087 (5)	0.067 (5)	0.090 (4)
C8B	0.078 (5)	0.034 (3)	0.074 (4)	0.010 (2)	0.023 (3)	0.017 (2)
C9B	0.084 (5)	0.040 (3)	0.079 (4)	0.011 (3)	0.026 (3)	0.022 (3)
C10B	0.068 (5)	0.048 (3)	0.080 (4)	0.019 (3)	0.024 (3)	0.020 (3)
O3B	0.096 (5)	0.194 (8)	0.145 (6)	0.052 (5)	0.052 (4)	0.113 (6)
O4B	0.132 (8)	0.140 (5)	0.131 (5)	0.087 (5)	0.067 (5)	0.090 (4)

Geometric parameters (Å, º)

S1—C4	1.801 (5)	C7—H7A	0.9700
S1—C3	1.808 (5)	C7—H7B	0.9700
S2—C8B	1.78 (3)	C8—C9	1.490 (8)
S2—C7	1.804 (5)	C8—H8A	0.9700
S2—C8	1.816 (6)	C8—H8B	0.9700
N1—C1	1.342 (5)	C9—C10	1.496 (8)
N1—C2^{i}	1.351 (5)	C9—H9A	0.9700
C1—C2	1.371 (6)	C9—H9B	0.9700
C1—C3	1.503 (5)	C10—O4	1.224 (8)
C2—C7	1.504 (6)	C10—O3	1.231 (9)
C3—H3A	0.9700	O4—H4O	0.8200
C3—H3B	0.9700	C8B—C9B	1.516 (19)
C4—C5	1.526 (8)	C8B—H8B1	0.9700
C4—H4A	0.9700	C8B—H8B2	0.9700
C4—H4B	0.9700	C9B—C10B	1.505 (19)
C5—C6	1.485 (7)	C9B—H9B1	0.9700
C5—H5A	0.9700	C9B—H9B2	0.9700
C5—H5B	0.9700	C10B—O3B	1.226 (19)
C6—O1	1.238 (7)	C10B—O4B	1.265 (19)
C6—O2	1.258 (8)	O4B—H4OB	0.8200
O2—H2O	0.8200		
C4—S1—C3	100.2 (2)	C2—C7—H7B	108.8
C8B—S2—C7	112.9 (9)	S2—C7—H7B	108.8
C7—S2—C8	96.8 (2)	H7A—C7—H7B	107.7
C1—N1—C2^{i}	117.9 (4)	C9—C8—S2	110.8 (4)
N1—C1—C2	121.2 (4)	C9—C8—H8A	109.5
N1—C1—C3	116.3 (4)	S2—C8—H8A	109.5
C2—C1—C3	122.5 (4)	C9—C8—H8B	109.5
N1^{i}—C2—C1	120.9 (4)	S2—C8—H8B	109.5
N1^{i}—C2—C7	115.7 (4)	H8A—C8—H8B	108.1
C1—C2—C7	123.5 (4)	C8—C9—C10	110.3 (5)
C1—C3—S1	113.3 (3)	C8—C9—H9A	109.6

C1—C3—H3A	108.9	C10—C9—H9A	109.6
S1—C3—H3A	108.9	C8—C9—H9B	109.6
C1—C3—H3B	108.9	C10—C9—H9B	109.6
S1—C3—H3B	108.9	H9A—C9—H9B	108.1
H3A—C3—H3B	107.7	O4—C10—O3	121.6 (7)
C5—C4—S1	112.3 (3)	O4—C10—C9	118.5 (7)
C5—C4—H4A	109.2	O3—C10—C9	119.8 (6)
S1—C4—H4A	109.2	C10—O4—H4O	109.5
C5—C4—H4B	109.2	C9B—C8B—S2	99.9 (19)
S1—C4—H4B	109.2	C9B—C8B—H8B1	111.8
H4A—C4—H4B	107.9	S2—C8B—H8B1	111.8
C6—C5—C4	113.3 (5)	C9B—C8B—H8B2	111.8
C6—C5—H5A	108.9	S2—C8B—H8B2	111.8
C4—C5—H5A	108.9	H8B1—C8B—H8B2	109.5
C6—C5—H5B	108.9	C10B—C9B—C8B	108 (2)
C4—C5—H5B	108.9	C10B—C9B—H9B1	110.0
H5A—C5—H5B	107.7	C8B—C9B—H9B1	110.0
O1—C6—O2	122.4 (5)	C10B—C9B—H9B2	110.0
O1—C6—C5	121.3 (5)	C8B—C9B—H9B2	110.0
O2—C6—C5	116.3 (6)	H9B1—C9B—H9B2	108.4
C6—O2—H2O	109.5	O3B—C10B—O4B	119 (3)
C2—C7—S2	113.8 (3)	O3B—C10B—C9B	126 (3)
C2—C7—H7A	108.8	O4B—C10B—C9B	110 (3)
S2—C7—H7A	108.8	C10B—O4B—H4OB	109.5

C2^{i}—N1—C1—C2	−0.6 (6)	N1^{i}—C2—C7—S2	103.4 (4)
C2^{i}—N1—C1—C3	179.3 (4)	C1—C2—C7—S2	−75.4 (5)
N1—C1—C2—N1^{i}	0.6 (7)	C8B—S2—C7—C2	−43.7 (10)
C3—C1—C2—N1^{i}	−179.3 (4)	C8—S2—C7—C2	−66.8 (4)
N1—C1—C2—C7	179.3 (4)	C7—S2—C8—C9	−178.1 (5)
C3—C1—C2—C7	−0.6 (6)	S2—C8—C9—C10	−172.5 (5)
N1—C1—C3—S1	98.8 (4)	C8—C9—C10—O4	−57.8 (10)
C2—C1—C3—S1	−81.3 (5)	C8—C9—C10—O3	120.5 (9)
C4—S1—C3—C1	−72.6 (4)	C7—S2—C8B—C9B	−87.0 (16)
C3—S1—C4—C5	−86.7 (4)	S2—C8B—C9B—C10B	177 (2)
S1—C4—C5—C6	−65.0 (6)	C8B—C9B—C10B—O3B	−8 (5)
C4—C5—C6—O1	−17.0 (8)	C8B—C9B—C10B—O4B	−164 (3)
C4—C5—C6—O2	165.7 (6)		

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O3^{ii}	0.82	1.94	2.66 (1)	146
O2—H2*O*···O3*B*^{ii}	0.82	2.20	2.77 (3)	127

O4—H4*O*···O1^{iii}	0.82	1.88	2.66 (1)	158
O4*B*—H4*OB*···O1^{iii}	0.82	1.86	2.67 (4)	170

Symmetry codes: (ii) *x*, *y*, *z*+1; (iii) *x*, *y*, *z*−1.

Poly[(*μ*-3-{[(3,5,6-tris{[(2-carboxyethyl)sulfanyl]methyl}pyrazin-2-yl)methyl]sulfanyl}propanoato)potassium] (KH3L1)

Crystal data

[K($C_{20}H_{27}N_2O_8S_4$)]
M_r = 590.77
Monoclinic, *C*2/*c*
a = 30.080 (4) Å
b = 8.4716 (10) Å
c = 9.5908 (12) Å
β = 94.717 (11)°
V = 2435.7 (6) Å^3
Z = 4
F(000) = 1232
D_x = 1.611 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 7965 reflections
θ = 1.4–25.0°
μ = 0.61 mm^{-1}
T = 153 K
Plate, colourless
0.50 × 0.50 × 0.10 mm

Data collection

STOE IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
φ + *ω* scans
Absorption correction: multi-scan (MULABS; Spek, 2020)
T_{min} = 0.640, T_{max} = 1.000
10309 measured reflections
2084 independent reflections
1646 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 24.8°, θ_{min} = 2.5°
h = −35→35
k = −9→9
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.106
S = 1.02
2084 reflections
165 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 1.5958P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
K1	0.500000	−0.28423 (13)	−0.250000	0.0357 (3)
S1	0.34409 (2)	−0.03261 (9)	0.17646 (7)	0.0305 (2)
S2	0.18978 (2)	−0.11089 (9)	0.16606 (8)	0.0342 (2)

O1	0.46781 (7)	−0.2235 (3)	0.0136 (2)	0.0404 (5)
O2	0.46330 (7)	−0.0466 (3)	0.1860 (2)	0.0402 (6)
H20	0.500000	−0.073 (9)	0.250000	0.12 (3)*
O3	0.06245 (6)	0.1153 (3)	−0.0544 (2)	0.0363 (5)
O4	0.03178 (7)	0.1057 (3)	0.1493 (2)	0.0472 (7)
H4O	0.0125 (17)	0.157 (7)	0.109 (5)	0.097 (19)*
N1	0.28457 (7)	0.2024 (3)	−0.0774 (2)	0.0240 (5)
C1	0.27160 (8)	0.1117 (3)	0.0267 (3)	0.0240 (6)
C2	0.23661 (8)	0.1606 (3)	0.1047 (3)	0.0229 (6)
C3	0.29578 (8)	−0.0422 (3)	0.0500 (3)	0.0280 (6)
H3A	0.305554	−0.079313	−0.040443	0.034*
H3B	0.274689	−0.121452	0.082227	0.034*
C4	0.38202 (9)	0.0765 (4)	0.0748 (3)	0.0352 (7)
H4A	0.364384	0.148969	0.010857	0.042*
H4B	0.401718	0.141946	0.139218	0.042*
C5	0.41100 (9)	−0.0265 (4)	−0.0116 (3)	0.0335 (7)
H5A	0.391756	−0.108161	−0.059355	0.040*
H5B	0.422744	0.040143	−0.084955	0.040*
C6	0.44979 (9)	−0.1079 (4)	0.0676 (3)	0.0326 (7)
C7	0.22055 (9)	0.0650 (3)	0.2220 (3)	0.0283 (6)
H7A	0.201211	0.132352	0.275893	0.034*
H7B	0.246620	0.033583	0.285664	0.034*
C8	0.14217 (9)	−0.0295 (4)	0.0628 (3)	0.0329 (7)
H8A	0.152427	0.055219	0.002031	0.039*
H8B	0.128312	−0.113189	0.001607	0.039*
C9	0.10744 (9)	0.0371 (4)	0.1528 (3)	0.0350 (7)
H9A	0.099826	−0.044379	0.220895	0.042*
H9B	0.120475	0.128185	0.206358	0.042*
C10	0.06542 (9)	0.0895 (4)	0.0702 (3)	0.0307 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0254 (4)	0.0547 (6)	0.0267 (5)	0.000	−0.0009 (3)	0.000
S1	0.0189 (3)	0.0428 (5)	0.0297 (4)	0.0034 (3)	0.0011 (3)	0.0042 (3)
S2	0.0224 (4)	0.0335 (4)	0.0466 (5)	−0.0003 (3)	0.0027 (3)	0.0034 (3)
O1	0.0302 (11)	0.0590 (15)	0.0320 (11)	0.0130 (10)	0.0022 (9)	−0.0023 (10)
O2	0.0246 (10)	0.0633 (15)	0.0319 (11)	0.0051 (10)	−0.0024 (9)	−0.0077 (10)
O3	0.0259 (10)	0.0554 (15)	0.0278 (11)	0.0021 (9)	0.0032 (8)	0.0038 (9)
O4	0.0266 (12)	0.0804 (19)	0.0356 (13)	0.0138 (12)	0.0085 (10)	0.0044 (12)
N1	0.0156 (10)	0.0304 (13)	0.0255 (12)	−0.0007 (9)	−0.0019 (9)	−0.0021 (10)
C1	0.0152 (12)	0.0299 (16)	0.0256 (14)	0.0007 (11)	−0.0048 (10)	−0.0038 (11)
C2	0.0159 (11)	0.0278 (15)	0.0239 (14)	−0.0009 (11)	−0.0036 (10)	−0.0026 (11)
C3	0.0187 (13)	0.0317 (16)	0.0331 (15)	0.0022 (11)	−0.0012 (11)	−0.0003 (12)
C4	0.0210 (13)	0.0424 (19)	0.0421 (18)	−0.0024 (13)	0.0018 (12)	0.0070 (14)
C5	0.0213 (13)	0.051 (2)	0.0280 (15)	−0.0009 (12)	0.0017 (12)	0.0039 (13)
C6	0.0185 (13)	0.053 (2)	0.0268 (15)	−0.0019 (13)	0.0047 (11)	0.0024 (14)
C7	0.0229 (14)	0.0366 (16)	0.0251 (14)	−0.0005 (12)	0.0013 (11)	0.0024 (12)

C8	0.0224 (14)	0.0422 (19)	0.0338 (16)	−0.0034 (12)	0.0011 (12)	−0.0009 (13)
C9	0.0208 (14)	0.056 (2)	0.0280 (15)	0.0017 (13)	0.0037 (12)	0.0032 (14)
C10	0.0217 (13)	0.0388 (18)	0.0321 (16)	−0.0033 (12)	0.0052 (12)	−0.0013 (13)

Geometric parameters (Å, º)

K1—O1	2.828 (2)	C1—C2	1.403 (4)
K1—O1^{i}	2.828 (2)	C1—C3	1.501 (4)
K1—O2^{ii}	3.056 (3)	C2—C7	1.498 (4)
K1—O2^{iii}	3.056 (3)	C3—H3A	0.9900
K1—O3^{iv}	2.682 (2)	C3—H3B	0.9900
K1—O3^{v}	2.682 (2)	C4—C5	1.525 (4)
K1—O4^{vi}	3.069 (3)	C4—H4A	0.9900
K1—O4^{vii}	3.069 (3)	C4—H4B	0.9900
S1—C4	1.814 (3)	C5—C6	1.506 (4)
S1—C3	1.816 (3)	C5—H5A	0.9900
S2—C8	1.809 (3)	C5—H5B	0.9900
S2—C7	1.812 (3)	C7—H7A	0.9900
O1—C6	1.252 (4)	C7—H7B	0.9900
O2—C6	1.284 (4)	C8—C9	1.517 (4)
O2—H20	1.239 (15)	C8—H8A	0.9900
O3—C10	1.211 (3)	C8—H8B	0.9900
O4—C10	1.321 (3)	C9—C10	1.502 (4)
O4—H4O	0.80 (5)	C9—H9A	0.9900
N1—C2^{viii}	1.339 (4)	C9—H9B	0.9900
N1—C1	1.343 (4)		

O3^{iv}—K1—O3^{v}	143.00 (11)	C1—C2—C7	122.9 (3)
O3^{iv}—K1—O1	114.30 (6)	C1—C3—S1	114.31 (19)
O3^{v}—K1—O1	72.78 (6)	C1—C3—H3A	108.7
O3^{iv}—K1—O1^{i}	72.78 (6)	S1—C3—H3A	108.7
O3^{v}—K1—O1^{i}	114.30 (6)	C1—C3—H3B	108.7
O1—K1—O1^{i}	159.05 (11)	S1—C3—H3B	108.7
O3^{iv}—K1—O2^{ii}	130.71 (7)	H3A—C3—H3B	107.6
O3^{v}—K1—O2^{ii}	85.98 (6)	C5—C4—S1	114.4 (2)
O1—K1—O2^{ii}	78.37 (7)	C5—C4—H4A	108.7
O1^{i}—K1—O2^{ii}	82.42 (6)	S1—C4—H4A	108.7
O3^{iv}—K1—O2^{iii}	85.98 (6)	C5—C4—H4B	108.7
O3^{v}—K1—O2^{iii}	130.71 (7)	S1—C4—H4B	108.7
O1—K1—O2^{iii}	82.42 (6)	H4A—C4—H4B	107.6
O1^{i}—K1—O2^{iii}	78.37 (7)	C6—C5—C4	116.2 (2)
O2^{ii}—K1—O2^{iii}	46.99 (8)	C6—C5—H5A	108.2
O3^{iv}—K1—O4^{vi}	73.54 (7)	C4—C5—H5A	108.2
O3^{v}—K1—O4^{vi}	73.75 (7)	C6—C5—H5B	108.2
O1—K1—O4^{vi}	125.54 (7)	C4—C5—H5B	108.2
O1^{i}—K1—O4^{vi}	75.02 (7)	H5A—C5—H5B	107.4
O2^{ii}—K1—O4^{vi}	139.50 (6)	O1—C6—O2	124.5 (3)
O2^{iii}—K1—O4^{vi}	150.17 (6)	O1—C6—C5	119.6 (3)

O3^{iv}—K1—O4^{vii}	73.75 (7)	O2—C6—C5	115.9 (3)
O3^{v}—K1—O4^{vii}	73.54 (7)	C2—C7—S2	114.24 (19)
O1—K1—O4^{vii}	75.02 (7)	C2—C7—H7A	108.7
O1^{i}—K1—O4^{vii}	125.54 (7)	S2—C7—H7A	108.7
O2^{ii}—K1—O4^{vii}	150.17 (6)	C2—C7—H7B	108.7
O2^{iii}—K1—O4^{vii}	139.50 (6)	S2—C7—H7B	108.7
O4^{vi}—K1—O4^{vii}	54.87 (9)	H7A—C7—H7B	107.6
C4—S1—C3	99.68 (14)	C9—C8—S2	112.4 (2)
C8—S2—C7	102.17 (14)	C9—C8—H8A	109.1
C6—O1—K1	134.73 (19)	S2—C8—H8A	109.1
C6—O2—K1^{ii}	129.17 (19)	C9—C8—H8B	109.1
C6—O2—H20	125 (2)	S2—C8—H8B	109.1
K1^{ii}—O2—H20	77 (4)	H8A—C8—H8B	107.9
C10—O3—K1^{ix}	137.58 (18)	C10—C9—C8	113.5 (2)
C10—O4—K1^{vii}	111.2 (2)	C10—C9—H9A	108.9
C10—O4—H4O	110 (4)	C8—C9—H9A	108.9
K1^{vii}—O4—H4O	114 (4)	C10—C9—H9B	108.9
C2^{viii}—N1—C1	118.6 (2)	C8—C9—H9B	108.9
N1—C1—C2	120.3 (2)	H9A—C9—H9B	107.7
N1—C1—C3	116.2 (2)	O3—C10—O4	123.4 (3)
C2—C1—C3	123.5 (2)	O3—C10—C9	124.3 (2)
N1^{viii}—C2—C1	121.1 (2)	O4—C10—C9	112.3 (2)
N1^{viii}—C2—C7	116.0 (2)		

C2^{viii}—N1—C1—C2	−0.1 (4)	K1^{ii}—O2—C6—C5	−60.6 (3)
C2^{viii}—N1—C1—C3	178.5 (2)	C4—C5—C6—O1	161.6 (3)
N1—C1—C2—N1^{viii}	0.1 (4)	C4—C5—C6—O2	−21.4 (4)
C3—C1—C2—N1^{viii}	−178.4 (2)	N1^{viii}—C2—C7—S2	107.9 (2)
N1—C1—C2—C7	180.0 (2)	C1—C2—C7—S2	−72.0 (3)
C3—C1—C2—C7	1.5 (4)	C8—S2—C7—C2	−62.3 (2)
N1—C1—C3—S1	91.6 (3)	C7—S2—C8—C9	−77.5 (2)
C2—C1—C3—S1	−89.8 (3)	S2—C8—C9—C10	−173.8 (2)
C4—S1—C3—C1	−72.3 (2)	K1^{ix}—O3—C10—O4	1.7 (5)
C3—S1—C4—C5	−90.3 (2)	K1^{ix}—O3—C10—C9	−177.7 (2)
S1—C4—C5—C6	−76.4 (3)	K1^{vii}—O4—C10—O3	110.5 (3)
K1—O1—C6—O2	−127.8 (3)	K1^{vii}—O4—C10—C9	−70.0 (3)
K1—O1—C6—C5	48.8 (4)	C8—C9—C10—O3	−17.9 (5)
K1^{ii}—O2—C6—O1	116.1 (3)	C8—C9—C10—O4	162.6 (3)

Symmetry codes: (i) −*x*+1, *y*, −*z*−1/2; (ii) −*x*+1, −*y*, −*z*; (iii) *x*, −*y*, *z*−1/2; (iv) −*x*+1/2, *y*−1/2, −*z*−1/2; (v) *x*+1/2, *y*−1/2, *z*; (vi) *x*+1/2, −*y*−1/2, *z*−1/2; (vii) −*x*+1/2, −*y*−1/2, −*z*; (viii) −*x*+1/2, −*y*+1/2, −*z*; (ix) *x*−1/2, *y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*O*···O1^{ix}	0.80 (5)	1.86 (5)	2.661 (3)	180 (7)
O2—H20···O2^{x}	1.24 (1)	1.24 (1)	2.436 (3)	159 (7)
C4—H4*A*···N1	0.99	2.52	3.340 (4)	140
C4—H4*B*···O3^{viii}	0.99	2.49	3.114 (4)	121

C5—H5*B*···O2^{iii}	0.99	2.60	3.467 (4)	146
C7—H7*B*···N1^{xi}	0.99	2.60	3.454 (4)	144
C9—H9*A*···O3^{xi}	0.99	2.58	3.465 (4)	149

Symmetry codes: (iii) $x, -y, z-1/2$; (viii) $-x+1/2, -y+1/2, -z$; (ix) $x-1/2, y+1/2, z$; (x) $-x+1, y, -z+1/2$; (xi) $x, -y, z+1/2$.

Poly[(μ-3,3′-{[(3,6-bis{[(2-carboxyethyl)sulfanyl]methyl}pyrazine-2,5-diyl)bis(methylene)]bis(sulfanediyl)}dipropionato)dipotassium] (K2H2L1)

Crystal data

$[K_2(C_{20}H_{26}N_2O_8S_4)]$
M_r = 628.87
Monoclinic, *C*2/*c*
a = 27.908 (2) Å
b = 8.2916 (6) Å
c = 11.3035 (9) Å
β = 94.753 (6)°
V = 2606.7 (3) Å^3
Z = 4
F(000) = 1304
D_x = 1.602 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 20250 reflections
θ = 1.8–29.6°
μ = 0.73 mm^{-1}
T = 153 K
Plate, colourless
0.50 × 0.50 × 0.05 mm

Data collection

STOE IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
φ + *ω* scans
Absorption correction: empirical (using intensity measurements) (*ShxAbs*; Spek, 2020)
T_{min} = 0.416, T_{max} = 0.803
19423 measured reflections
3646 independent reflections
3175 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 29.6°, θ_{min} = 2.6°
h = −38→38
k = −11→11
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.103
S = 1.05
3646 reflections
167 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 3.5192P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.76 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
K1	0.000000	0.82906 (7)	0.750000	0.02908 (13)

K2	0.000000	0.64758 (6)	0.250000	0.02585 (12)
S1	0.15530 (2)	0.94369 (6)	0.36528 (5)	0.03200 (12)
S2	0.31454 (2)	0.91861 (6)	0.30731 (4)	0.02972 (12)
O1	0.03202 (5)	0.90961 (16)	0.37679 (12)	0.0288 (3)
O2	0.03173 (4)	0.75961 (15)	0.53962 (10)	0.0251 (2)
O3	0.44445 (5)	1.07891 (16)	0.64145 (11)	0.0264 (3)
O4	0.45504 (4)	1.14483 (16)	0.45457 (11)	0.0246 (2)
H4O	0.4811 (7)	1.187 (3)	0.485 (2)	0.037*
N1	0.22122 (5)	1.18192 (18)	0.58094 (13)	0.0226 (3)
C1	0.23166 (6)	1.10103 (19)	0.48370 (15)	0.0214 (3)
C2	0.26072 (6)	1.1694 (2)	0.40166 (14)	0.0214 (3)
C3	0.20952 (6)	0.9373 (2)	0.46641 (17)	0.0261 (3)
H3A	0.201509	0.894439	0.544105	0.031*
H3B	0.233073	0.863252	0.434300	0.031*
C4	0.11775 (7)	1.0635 (2)	0.4543 (2)	0.0344 (4)
H4A	0.138286	1.142471	0.500499	0.041*
H4B	0.094632	1.125024	0.400576	0.041*
C5	0.08989 (6)	0.9666 (2)	0.53952 (18)	0.0301 (4)
H5A	0.112007	0.889825	0.583250	0.036*
H5B	0.077277	1.040676	0.598231	0.036*
C6	0.04848 (6)	0.8740 (2)	0.47738 (14)	0.0215 (3)
C7	0.27238 (6)	1.0859 (2)	0.28997 (15)	0.0260 (3)
H7A	0.285609	1.166910	0.237196	0.031*
H7B	0.241998	1.045256	0.249183	0.031*
C8	0.37036 (6)	1.0182 (3)	0.35882 (16)	0.0295 (4)
H8A	0.397073	0.966995	0.320275	0.035*
H8B	0.368597	1.132425	0.333262	0.035*
C9	0.38174 (6)	1.0126 (2)	0.49202 (15)	0.0243 (3)
H9A	0.380284	0.899037	0.518480	0.029*
H9B	0.356583	1.073093	0.530128	0.029*
C10	0.43036 (6)	1.08130 (19)	0.53492 (14)	0.0216 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0442 (3)	0.0240 (2)	0.0186 (2)	0.000	−0.0001 (2)	0.000
K2	0.0356 (3)	0.0230 (2)	0.0189 (2)	0.000	0.00191 (18)	0.000
S1	0.0250 (2)	0.0304 (2)	0.0399 (3)	−0.00503 (16)	−0.00202 (17)	−0.00557 (18)
S2	0.0236 (2)	0.0297 (2)	0.0355 (2)	−0.00158 (16)	0.00042 (16)	−0.00746 (17)
O1	0.0311 (6)	0.0272 (6)	0.0269 (6)	−0.0064 (5)	−0.0040 (5)	0.0023 (5)
O2	0.0235 (5)	0.0282 (6)	0.0233 (5)	−0.0027 (5)	0.0009 (4)	0.0005 (5)
O3	0.0276 (6)	0.0300 (6)	0.0217 (5)	−0.0011 (5)	0.0019 (4)	0.0021 (5)
O4	0.0228 (5)	0.0299 (6)	0.0212 (5)	−0.0051 (5)	0.0024 (4)	0.0004 (5)
N1	0.0196 (6)	0.0235 (6)	0.0242 (6)	−0.0010 (5)	−0.0004 (5)	0.0030 (5)
C1	0.0173 (6)	0.0206 (7)	0.0256 (7)	−0.0002 (5)	−0.0027 (5)	0.0020 (6)
C2	0.0183 (7)	0.0230 (7)	0.0223 (7)	0.0002 (5)	−0.0022 (5)	0.0019 (6)
C3	0.0214 (7)	0.0213 (7)	0.0353 (9)	−0.0017 (6)	0.0007 (6)	0.0016 (6)
C4	0.0220 (8)	0.0231 (8)	0.0576 (12)	−0.0023 (6)	−0.0009 (8)	−0.0060 (8)

C5	0.0230 (8)	0.0295 (9)	0.0368 (9)	−0.0023 (6)	−0.0035 (7)	−0.0092 (7)
C6	0.0180 (7)	0.0212 (7)	0.0250 (7)	0.0004 (5)	0.0006 (5)	−0.0046 (6)
C7	0.0250 (8)	0.0290 (8)	0.0237 (7)	−0.0007 (6)	−0.0005 (6)	−0.0005 (6)
C8	0.0211 (7)	0.0402 (10)	0.0271 (8)	−0.0049 (7)	0.0021 (6)	−0.0020 (7)
C9	0.0218 (7)	0.0250 (8)	0.0261 (7)	−0.0017 (6)	0.0025 (6)	−0.0010 (6)
C10	0.0224 (7)	0.0205 (7)	0.0220 (7)	0.0019 (5)	0.0031 (6)	−0.0003 (5)

Geometric parameters (Å, º)

K1—O1^{i}	2.7084 (14)	O1—C6	1.227 (2)
K1—O1^{ii}	2.7084 (14)	O4—C10	1.296 (2)
K1—O2	2.6682 (12)	O4—H4O	0.855 (16)
K1—O2^{iii}	2.6683 (12)	O3—C10	1.236 (2)
K1—O3^{iv}	2.8099 (14)	N1—C1	1.340 (2)
K1—O3^{v}	2.8099 (13)	N1—C2^{xi}	1.341 (2)
K1—C6^{iii}	3.4864 (17)	C1—C2	1.401 (2)
K1—C6	3.4865 (17)	C1—C3	1.498 (2)
K1—K2^{vi}	3.9521 (8)	C2—C7	1.499 (2)
K1—K2^{ii}	4.3395 (8)	C3—H3A	0.9900
K2—O1^{vii}	2.7131 (13)	C3—H3B	0.9900
K2—O1	2.7132 (13)	C4—C5	1.518 (3)
K2—O3^{viii}	2.6683 (13)	C4—H4A	0.9900
K2—O3^{ix}	2.6682 (13)	C4—H4B	0.9900
K2—O4^{x}	2.7209 (12)	C5—C6	1.511 (2)
K2—O4^{iv}	2.7209 (12)	C5—H5A	0.9900
K2—C6^{vii}	3.3739 (16)	C5—H5B	0.9900
K2—C6	3.3739 (16)	C7—H7A	0.9900
K2—C10^{viii}	3.5364 (16)	C7—H7B	0.9900
K2—C10^{ix}	3.5364 (16)	C8—C9	1.513 (2)
S1—C4	1.809 (2)	C8—H8A	0.9900
S1—C3	1.8200 (18)	C8—H8B	0.9900
S2—C8	1.8159 (18)	C9—C10	1.514 (2)
S2—C7	1.8190 (19)	C9—H9A	0.9900
O2—C6	1.291 (2)	C9—H9B	0.9900

O2—K1—O2^{iii}	155.07 (6)	O3^{ix}—K2—K1^{vi}	45.27 (3)
O2—K1—O1^{i}	121.67 (4)	O1^{vii}—K2—K1^{vi}	143.21 (3)
O2^{iii}—K1—O1^{i}	79.65 (4)	O1—K2—K1^{vi}	143.21 (3)
O2—K1—O1^{ii}	79.65 (4)	O4^{x}—K2—K1^{vi}	89.52 (3)
O2^{iii}—K1—O1^{ii}	121.67 (4)	O4^{iv}—K2—K1^{vi}	89.52 (3)
O1^{i}—K1—O1^{ii}	73.73 (6)	C6^{vii}—K2—K1^{vi}	123.80 (3)
O2—K1—O3^{iv}	70.32 (4)	C6—K2—K1^{vi}	123.80 (3)
O2^{iii}—K1—O3^{iv}	91.03 (4)	C10^{viii}—K2—K1^{vi}	57.55 (3)
O1^{i}—K1—O3^{iv}	165.36 (4)	C10^{ix}—K2—K1^{vi}	57.55 (3)
O1^{ii}—K1—O3^{iv}	102.33 (4)	O3^{viii}—K2—K1^{ii}	134.73 (3)
O2—K1—O3^{v}	91.03 (4)	O3^{ix}—K2—K1^{ii}	134.73 (3)
O2^{iii}—K1—O3^{v}	70.32 (4)	O1^{vii}—K2—K1^{ii}	36.79 (3)
O1^{i}—K1—O3^{v}	102.33 (4)	O1—K2—K1^{ii}	36.79 (3)

O1^{ii}—K1—O3^{v}	165.36 (4)	O4^{x}—K2—K1^{ii}	90.48 (3)
O3^{iv}—K1—O3^{v}	84.85 (5)	O4^{iv}—K2—K1^{ii}	90.48 (3)
O2—K1—C6^{iii}	172.97 (4)	C6^{vii}—K2—K1^{ii}	56.20 (3)
O2^{iii}—K1—C6^{iii}	18.84 (4)	C6—K2—K1^{ii}	56.20 (3)
O1^{i}—K1—C6^{iii}	65.30 (4)	C10^{viii}—K2—K1^{ii}	122.45 (3)
O1^{ii}—K1—C6^{iii}	104.31 (4)	C10^{ix}—K2—K1^{ii}	122.45 (3)
O3^{iv}—K1—C6^{iii}	102.96 (4)	K1^{vi}—K2—K1^{ii}	180.0
O3^{v}—K1—C6^{iii}	86.17 (4)	C4—S1—C3	99.00 (9)
O2—K1—C6	18.84 (4)	C8—S2—C7	102.58 (9)
O2^{iii}—K1—C6	172.97 (4)	C6—O2—K1	119.28 (10)
O1^{i}—K1—C6	104.31 (4)	C6—O1—K1^{ii}	139.92 (11)
O1^{ii}—K1—C6	65.30 (4)	C6—O1—K2	112.22 (11)
O3^{iv}—K1—C6	86.17 (4)	K1^{ii}—O1—K2	106.34 (4)
O3^{v}—K1—C6	102.96 (4)	C10—O4—K2^{xii}	155.24 (11)
C6^{iii}—K1—C6	167.74 (6)	C10—O4—H4O	111.3 (17)
O2—K1—K2^{vi}	77.54 (3)	K2^{xii}—O4—H4O	84.7 (17)
O2^{iii}—K1—K2^{vi}	77.54 (3)	C10—O3—K2^{ix}	125.83 (11)
O1^{i}—K1—K2^{vi}	143.13 (3)	C10—O3—K1^{xii}	122.23 (11)
O1^{ii}—K1—K2^{vi}	143.13 (3)	K2^{ix}—O3—K1^{xii}	92.31 (4)
O3^{iv}—K1—K2^{vi}	42.42 (3)	C1—N1—C2^{xi}	118.43 (14)
O3^{v}—K1—K2^{vi}	42.42 (3)	N1—C1—C2	121.17 (15)
C6^{iii}—K1—K2^{vi}	96.13 (3)	N1—C1—C3	116.44 (15)
C6—K1—K2^{vi}	96.13 (3)	C2—C1—C3	122.37 (15)
O2—K1—K2^{ii}	102.46 (3)	N1^{xi}—C2—C1	120.40 (15)
O2^{iii}—K1—K2^{ii}	102.46 (3)	N1^{xi}—C2—C7	116.30 (15)
O1^{i}—K1—K2^{ii}	36.87 (3)	C1—C2—C7	123.28 (15)
O1^{ii}—K1—K2^{ii}	36.87 (3)	C1—C3—S1	111.60 (12)
O3^{iv}—K1—K2^{ii}	137.58 (3)	C1—C3—H3A	109.3
O3^{v}—K1—K2^{ii}	137.58 (3)	S1—C3—H3A	109.3
C6^{iii}—K1—K2^{ii}	83.87 (3)	C1—C3—H3B	109.3
C6—K1—K2^{ii}	83.87 (3)	S1—C3—H3B	109.3
K2^{vi}—K1—K2^{ii}	180.0	H3A—C3—H3B	108.0
O3^{viii}—K2—O3^{ix}	90.54 (6)	C5—C4—S1	114.41 (14)
O3^{viii}—K2—O1^{vii}	99.63 (4)	C5—C4—H4A	108.7
O3^{ix}—K2—O1^{vii}	163.72 (4)	S1—C4—H4A	108.7
O3^{viii}—K2—O1	163.72 (4)	C5—C4—H4B	108.7
O3^{ix}—K2—O1	99.63 (4)	S1—C4—H4B	108.7
O1^{vii}—K2—O1	73.59 (6)	H4A—C4—H4B	107.6
O3^{viii}—K2—O4^{x}	83.95 (4)	C6—C5—C4	112.73 (16)
O3^{ix}—K2—O4^{x}	95.38 (4)	C6—C5—H5A	109.0
O1^{vii}—K2—O4^{x}	73.30 (4)	C4—C5—H5A	109.0
O1—K2—O4^{x}	107.50 (4)	C6—C5—H5B	109.0
O3^{viii}—K2—O4^{iv}	95.38 (4)	C4—C5—H5B	109.0
O3^{ix}—K2—O4^{iv}	83.95 (4)	H5A—C5—H5B	107.8
O1^{vii}—K2—O4^{iv}	107.50 (4)	O1—C6—O2	123.88 (15)
O1—K2—O4^{iv}	73.30 (4)	O1—C6—C5	121.42 (16)
O4^{x}—K2—O4^{iv}	179.04 (6)	O2—C6—C5	114.67 (15)
O3^{viii}—K2—C6^{vii}	81.96 (4)	O1—C6—K2	48.11 (8)

O3^{ix}—K2—C6^{vii}	157.35 (4)	O2—C6—K2	82.31 (9)
O1^{vii}—K2—C6^{vii}	19.67 (4)	C5—C6—K2	151.60 (11)
O1—K2—C6^{vii}	92.90 (4)	O1—C6—K1	134.60 (11)
O4^{x}—K2—C6^{vii}	62.69 (4)	O2—C6—K1	41.88 (8)
O4^{iv}—K2—C6^{vii}	117.91 (4)	C5—C6—K1	88.93 (10)
O3^{viii}—K2—C6	157.35 (4)	K2—C6—K1	116.96 (5)
O3^{ix}—K2—C6	81.96 (4)	C2—C7—S2	116.42 (12)
O1^{vii}—K2—C6	92.90 (4)	C2—C7—H7A	108.2
O1—K2—C6	19.67 (4)	S2—C7—H7A	108.2
O4^{x}—K2—C6	117.91 (4)	C2—C7—H7B	108.2
O4^{iv}—K2—C6	62.69 (4)	S2—C7—H7B	108.2
C6^{vii}—K2—C6	112.40 (6)	H7A—C7—H7B	107.3
O3^{viii}—K2—C10^{viii}	16.46 (4)	C9—C8—S2	114.13 (13)
O3^{ix}—K2—C10^{viii}	101.75 (4)	C9—C8—H8A	108.7
O1^{vii}—K2—C10^{viii}	85.89 (4)	S2—C8—H8A	108.7
O1—K2—C10^{viii}	158.61 (4)	C9—C8—H8B	108.7
O4^{x}—K2—C10^{viii}	71.16 (4)	S2—C8—H8B	108.7
O4^{iv}—K2—C10^{viii}	108.29 (4)	H8A—C8—H8B	107.6
C6^{vii}—K2—C10^{viii}	67.17 (4)	C8—C9—C10	114.57 (14)
C6—K2—C10^{viii}	170.09 (4)	C8—C9—H9A	108.6
O3^{viii}—K2—C10^{ix}	101.75 (4)	C10—C9—H9A	108.6
O3^{ix}—K2—C10^{ix}	16.46 (4)	C8—C9—H9B	108.6
O1^{vii}—K2—C10^{ix}	158.61 (4)	C10—C9—H9B	108.6
O1—K2—C10^{ix}	85.89 (4)	H9A—C9—H9B	107.6
O4^{x}—K2—C10^{ix}	108.29 (4)	O3—C10—O4	122.99 (16)
O4^{iv}—K2—C10^{ix}	71.16 (4)	O3—C10—C9	120.71 (15)
C6^{vii}—K2—C10^{ix}	170.09 (4)	O4—C10—C9	116.27 (14)
C6—K2—C10^{ix}	67.17 (4)	O3—C10—K2^{ix}	37.72 (8)
C10^{viii}—K2—C10^{ix}	115.09 (5)	O4—C10—K2^{ix}	113.96 (10)
O3^{viii}—K2—K1^{vi}	45.27 (3)	C9—C10—K2^{ix}	116.44 (10)
C2^{xi}—N1—C1—C2	0.0 (2)	C4—C5—C6—O1	−18.7 (2)
C2^{xi}—N1—C1—C3	−178.32 (14)	C4—C5—C6—O2	162.94 (15)
N1—C1—C2—N1^{xi}	0.0 (3)	C4—C5—C6—K2	40.3 (3)
C3—C1—C2—N1^{xi}	178.22 (14)	C4—C5—C6—K1	−162.96 (14)
N1—C1—C2—C7	−178.30 (15)	N1^{xi}—C2—C7—S2	108.63 (15)
C3—C1—C2—C7	−0.1 (2)	C1—C2—C7—S2	−72.98 (19)
N1—C1—C3—S1	97.64 (16)	C8—S2—C7—C2	−67.34 (15)
C2—C1—C3—S1	−80.62 (18)	C7—S2—C8—C9	97.89 (15)
C4—S1—C3—C1	−65.81 (15)	S2—C8—C9—C10	174.51 (12)
C3—S1—C4—C5	−87.72 (15)	K2^{ix}—O3—C10—O4	−87.24 (18)
S1—C4—C5—C6	−73.29 (18)	K1^{xii}—O3—C10—O4	33.7 (2)
K1^{ii}—O1—C6—O2	128.23 (16)	K2^{ix}—O3—C10—C9	94.51 (17)
K2—O1—C6—O2	−35.0 (2)	K1^{xii}—O3—C10—C9	−144.57 (12)
K1^{ii}—O1—C6—C5	−49.9 (3)	K1^{xii}—O3—C10—K2^{ix}	120.92 (16)
K2—O1—C6—C5	146.80 (13)	K2^{xii}—O4—C10—O3	125.1 (2)
K1^{ii}—O1—C6—K2	163.2 (2)	K2^{xii}—O4—C10—C9	−56.6 (3)
K1^{ii}—O1—C6—K1	74.9 (2)	K2^{xii}—O4—C10—K2^{ix}	83.1 (3)

K2—O1—C6—K1	−88.34 (15)	C8—C9—C10—O3	−177.68 (16)
K1—O2—C6—O1	−121.20 (15)	C8—C9—C10—O4	3.9 (2)
K1—O2—C6—C5	57.09 (17)	C8—C9—C10—K2^{ix}	−134.75 (13)
K1—O2—C6—K2	−146.73 (7)		

Symmetry codes: (i) *x*, −*y*+2, *z*+1/2; (ii) −*x*, −*y*+2, −*z*+1; (iii) −*x*, *y*, −*z*+3/2; (iv) *x*−1/2, *y*−1/2, *z*; (v) −*x*+1/2, *y*−1/2, −*z*+3/2; (vi) −*x*, −*y*+1, −*z*+1; (vii) −*x*, *y*, −*z*+1/2; (viii) *x*−1/2, −*y*+3/2, *z*−1/2; (ix) −*x*+1/2, −*y*+3/2, −*z*+1; (x) −*x*+1/2, *y*−1/2, −*z*+1/2; (xi) −*x*+1/2, −*y*+5/2, −*z*+1; (xii) *x*+1/2, *y*+1/2, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*O*···O2^{xii}	0.85 (2)	1.61 (2)	2.4637 (16)	177 (3)
C4—H4*A*···N1	0.99	2.44	3.266 (2)	141
C8—H8*A*···O3^{xiii}	0.99	2.53	3.436 (2)	151

Symmetry codes: (xii) *x*+1/2, *y*+1/2, *z*; (xiii) *x*, −*y*+2, *z*−1/2.