On the deprotonation of chlorothiazide

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Three alkali metal salt forms of the diuretic chlorothiazide (systematic name: 6-chloro-1,1-dioxo-2H-1,2,4-benzothiazine-7-sulfonamide, HCTZ) are described. When crystallized from aqueous solution, the Na and K salts, namely, poly-[[μ-aqua-aqua(μ_3-6-chloro-1,1-dioxo-7-sulfamoyl-2H-1,2,4-benzothiadiazin-2-ido)sodium] hemihydrate], $\{[Na(C_7H_5ClN_3O_4S_2)(H_2O)_2]\cdot0.5H_2O\}_n$, and poly-[[diaqua($\mu_5$-6-chloro-1,1-dioxo-7-sulfamoyl-2H-1,2,4-benzothiadiazin-2-ido)-potassium] hemihydrate], $\{[K(C_7H_5ClN_3O_4S_2)(H_2O)_2]\cdot0.5H_2O\}_n$, are both found to have stoichiometry MCTZ·2.5H$_2$O, with CTZ deprotonated at a heterocyclic ring N atom. Both the stoichiometry and the deprotonation site are different to those described in previously published versions of these structures. The Cs salt form is found to be the monohydrate CsCTZ·H$_2$O, namely, poly[[aqua(μ_5-6-chloro-1,1-dioxo-7-sulfamoyl-2H-1,2,4-benzothiadiazin-2-ido)caesium], $[Cs-(C_7H_5ClN_3O_4S_2)(H_2O)]_n$. As with the Na and K cognates, this structure is also deprotonated at the heterocyclic ring. NaCTZ is found to be a two-dimensional coordination polymer with bridges between Na centres formed by H$_2$O and SO$_2$ groups, and by links through the length of the coordinated CTZ anions. Water ligands in KCTZ and CsCTZ are terminal, rather than bridging between metal centres, but both compounds form structures where M—Cl interactions link two-dimensional motifs formed *via* M—O bonds (and in CsCTZ, M—N bonds) into three-dimensional coordination polymers.

1. Introduction

The active pharmaceutical ingredient (API) chlorothiazide and its sodium salt (NaCTZ, where CTZ is the 6-chloro-1,1-dioxo-7-sulfamoyl-2H-1,2,4-benzothiadiazin-2-ide anion) are sulfonamide compounds utilized as diuretic and antihypertensive drugs (Martins *et al.*, 2022; Steuber *et al.*, 2020). Chlorothiazide has also been widely used as a model API in crystallization studies. These studies have identified two polymorphs under ambient conditions and an additional high-pressure polymorphic form of chlorothiazide (Shankland *et al.*, 1997; Brydson & Kennedy, 2024; Oswald *et al.*, 2010), as well as numerous solvate and cocrystal forms (*e.g.* Johnston *et al.*, 2011; Aljohani *et al.*, 2017; Teng *et al.*, 2020). Despite this widespread study, and despite NaCTZ being used as an injectable form of the drug (Hankins *et al.*, 2001), only four structures of salt forms of chlorothiazide have been reported. These are APUZER [Cambridge Structural Database (CSD, Version 5.45 with updates to June 2024) refcode; Groom *et al.*, 2016], which was reported as a trihydrate form of NaCTZ (Paluch *et al.*, 2010), APUZIV and APUZOB which were, respectively, reported as the dihydrate and the mixed hydrate/ethanolate forms of KCTZ (Paluch *et al.*, 2011), and VEKBOF, which has the organic cation PhC(NH$_2$)$_2$ (Aljohani *et al.*, 2017). The alkali metal salt forms are of particular pharmaceutical interest, as they are reported to have aqueous
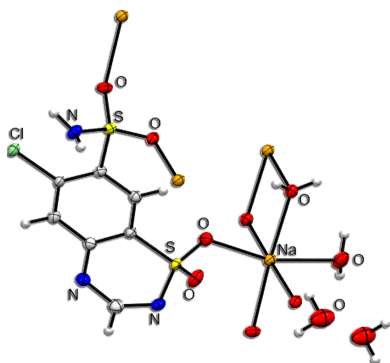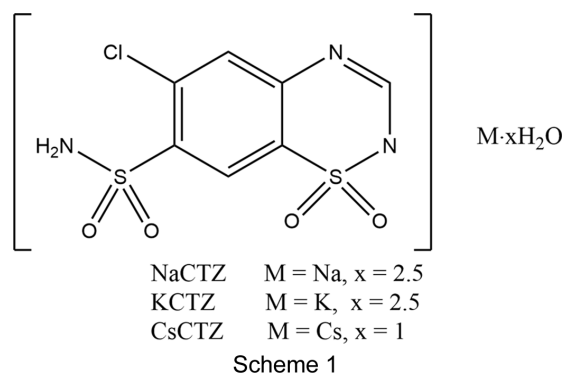
Table 1
Experimental details.

Experiments were carried out at 100 K with Cu $K\alpha$ radiation using a Rigaku Synergy-i diffractometer. H atoms were treated by a mixture of independent and constrained refinement.

	NaCTZ	KCTZ	CsCTZ
Crystal data			
Chemical formula	[Na(C$_7$H$_5$ClN$_3$O$_4$S$_2$)-(H$_2$O)$_2$]·0.5H$_2$O	[Na(C$_7$H$_5$ClN$_3$O$_4$S$_2$)-(H$_2$O)$_2$]·0.5H$_2$O	[Cs(C$_7$H$_5$ClN$_3$O$_4$S$_2$)(H$_2$O)]
M_r	362.74	378.85	445.64
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $C2/c$	Triclinic, $P\bar{1}$
a, b, c (Å)	8.3728 (7), 9.0819 (8), 9.6533 (6)	18.3139 (2), 7.3622 (1), 19.9670 (2)	7.71260 (1), 9.05930 (1), 10.13810 (1)
α, β, γ (°)	83.013 (6), 74.055 (6), 70.189 (7)	90, 99.734 (1), 90	93.9760 (1), 107.5390 (1), 107.8000 (1)
V (Å^3)	663.70 (10)	2653.40 (5)	632.84 (1)
Z	2	8	2
μ (mm^{-1})	6.16	8.66	28.08
Crystal size (mm)	0.13 × 0.11 × 0.05	0.16 × 0.15 × 0.05	0.24 × 0.15 × 0.12
Data collection			
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2019)	Gaussian (*CrysAlis PRO*; Rigaku OD, 2019)
T_{min}, T_{max}	0.587, 1.000	0.446, 1.000	0.022, 0.247
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10937, 2522, 2427	13919, 2543, 2503	14718, 2436, 2433
R_{int}	0.045	0.022	0.059
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.616	0.615	0.614
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.121, 1.06	0.022, 0.062, 1.07	0.036, 0.095, 1.11
No. of reflections	2522	2543	2436
No. of parameters	210	215	188
No. of restraints	8	9	5
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.87, −0.45	0.48, −0.38	1.75, −1.53

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2015a), *SHELXL2018* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *SHELXL* in *WinGX* (Farrugia, 2012).

solubilities that are orders of magnitude greater than that of chlorothiazide itself (Paluch *et al.*, 2010, 2011).

NaCTZ   M = Na, x = 2.5
KCTZ   M = K, x = 2.5
CsCTZ   M = Cs, x = 1
Scheme 1

Our attention was originally drawn to APUZER as its two-dimensional diagram in the CSD features a neutral CTZ ligand with the charge on Na$^+$ being balanced by a hydroxide ligand. Examining the associated CIF and the original article quickly showed that this was a transcription error (Paluch *et al.*, 2010). However, the anionic form of CTZ that is reported is in itself unusual. The structure given shows deprotonation of the SO$_2$NH$_2$ group and a proton present on the thiadiazine ring N atom adjacent to the ring SO$_2$ group. This is unusual as

the SO$_2$NH$_2$ group should be less acidic that the ring N—H group, and the solid-state structures of neutral CTZ forms invariably report the tautomer with the heterocyclic ring protonated at the N atom *para* to the SO$_2$ functionality (*e.g.* Brydson & Kennedy, 2024; Johnston *et al.*, 2011; Aljohani *et al.*, 2017). The KCTZ salt forms APUZIV and APUZOB are reported to have the same deprotonation pattern as APUZER (Paluch *et al.*, 2011), but the organic salt VEKBOF has a CTZ anion with the more intuitive deprotonation of the N—H group of the heterocyclic ring and retention of the SO$_2$NH$_2$ group (Aljohani *et al.*, 2017).

It is noted that the H-atom modelling in the reported structures of all three alkali metal salt forms has some problems. Notably, some H atoms on water molecules are missing, some refined N—H distances are unreasonably short (*e.g.* 0.65 Å), and those O—H and N—H bond lengths that are reasonable have all been fixed at the distances given. As incorrect H-atom positions are a known pitfall even for relatively high-quality crystal structure determinations (Seidel, 2018; Kennedy *et al.*, 2023; Bernal & Watkins, 2013; Raymond & Girolami, 2023; Harlow, 1996), we investigated the deprotonation of CTZ by redetermining the structures of the hydrated NaCTZ and KCTZ forms and by determining a related new structure – that of a monohydrated form of CsCTZ.

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2. Experimental

2.1. Synthesis and crystallization

The triclinic polymorph of CTZ was purchased from Thermo Scientific. Crystals of NaCTZ were prepared according to the aqueous method of Paluch *et al.* (2010). Crystals of KCTZ were prepared by adding excess KCl to an aqueous solution of NaCTZ, followed by slow evaporation of the solvent. For the preparation of CsCTZ, CTZ (0.10 g, 0.34 mmol) was dissolved in the minimum amount of a 1:1 (*v*/*v*) acetone–water mix. To this was added CsOH·H$_2$O (0.06 g, 0.36 mmol) dissolved in the minimum amount of water. After stirring and heating, the resulting solution was left to evaporate for 3 d at room temperature. This gave crystals of CsCTZ in approximately 50% yield. FT–IR (cm^{-1}); 3422, 3308, 3258, 3082, 2959, 1602, 1573, 1509, 1466, 1300, 1246, 1152, 1094, 956, 893, 714, 674, 614, 524.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were observed by difference synthesis, except for those of the disordered water molecule of NaCTZ. The H atoms of this latter group were thus placed in positions calculated so as to give sensible intermolecular hydrogen-bonding interactions. H atoms bound to C atoms were placed in expected geometric positions and treated in riding modes, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). Well-ordered H atoms bound to N or to O atoms were placed as found and refined isotropically with N/O—H distances restrained to 0.88 (1) Å.

3. Results and discussion

The core structures of NaCTZ, KCTZ and CsCTZ as newly determined herein are shown in Figs. 1–3 and key crystallographic parameters are given in Table 1. Paluch *et al.* (2010) modelled the structure of NaCTZ in APUZER (CSD refcode) as a trihydrate, with two water ligands coordinated to sodium and one free water molecule 'of solvation'. Both in the original article and in our hands, using this model gives the free water molecule an extremely large displacement ellipsoid and results in an O···O separation of just 1.482 Å between two free water molecule sites related by a centre of symmetry. In our current model, we thus treat this site, O3*W*, as a half-occupancy water molecule. This gives normal displacement ellipsoids, removes the erroneous O···O separation and reinterprets the structure as NaCTZ·2.5H$_2$O. In the text of Paluch *et al.* (2011), KCTZ (APUZIV) is described as a dihydrate form. However, both the CIF file deposited for APUZIV and our redetermination show that, similar to the Na salt, the K salt has stoichiometry KCTZ·2.5H$_2$O. Note that for both NaCTZ and KCTZ, a water content of 2.5 water molecules per cation is closer to the reported TGA derived water contents than are the alternative descriptions of these structures (Paluch *et al.*, 2010, 2011).

In both the original structures of NaCTZ and KCTZ (APUZER and APUZIV), some water H atoms were omitted, a H atom was placed on a heterocyclic N atom and the

Figure 1
Contents of the asymmetric unit of NaCTZ, expanded so as to show all metal-to-ligand coordination bonds. Note that here and elsewhere, non-H atoms are drawn as 50% probability ellipsoids and H atoms as small spheres of arbitrary size. See supporting information for full details of bonding contacts, including symmetry operations, for all structures.

pendant arm was modelled as the deprotonated SO$_2$NH group (Paluch *et al.*, 2010, 2011). In the current work, all the H atoms were observed in difference syntheses maps, with the exceptions of the H atoms of the disordered half-occupancy water molecule of NaCTZ. Adding the H atoms in the observed positions and modelling freely and isotropically gave structurally sensible H-atom positions for the water molecules and gave CTZ anions that had intact SO$_2$NH$_2$ groups and no protons on the heterocyclic N atoms. Moreover, there were no electron-density features suggesting any degree of protonation of the heterocyclic N atoms. Difference electron-density
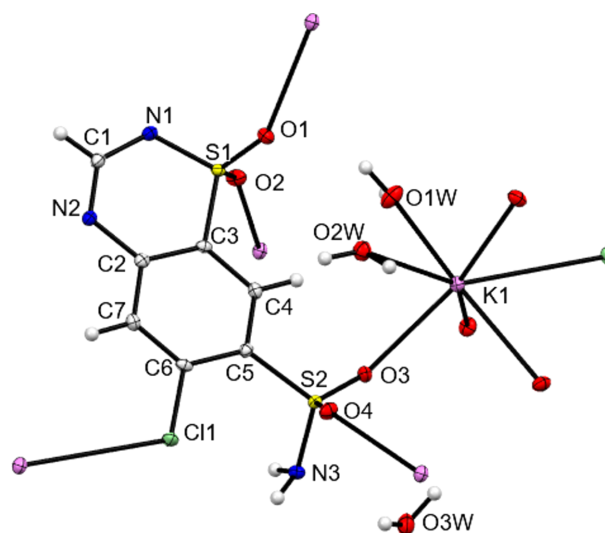

Figure 2
Contents of the asymmetric unit of KCTZ, expanded so as to show all metal-to-ligand coordination bonds.

Table 2
Hydrogen-bond geometry (Å, °) for NaCTZ.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N$\cdots$O2W^i	0.88 (1)	2.02 (1)	2.888 (3)	170 (4)
N3—H2N$\cdots$N1^{ii}	0.88 (1)	2.10 (1)	2.969 (3)	173 (4)
O1W—H1W$\cdots$N2^{iii}	0.87 (1)	1.91 (1)	2.778 (3)	171 (3)
O1W—H2W$\cdots$O2^i	0.87 (1)	2.29 (1)	3.148 (3)	169 (4)
O2W—H3W$\cdots$O1^{iv}	0.87 (1)	2.07 (2)	2.895 (3)	160 (4)
O2W—H4W$\cdots$O3W	0.87 (1)	1.97 (2)	2.797 (6)	158 (4)
O2W—H4W$\cdots$O3W^v	0.87 (1)	2.20 (3)	2.915 (6)	139 (3)
O3W—H5W$\cdots$O2^{vi}	0.95	1.90	2.853 (5)	180
O3W—H6W$\cdots$Cl1^{vii}	0.92	2.76	3.683 (5)	180

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

Table 3
Hydrogen-bond geometry (Å, °) for KCTZ.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N$\cdots$Cl1	0.87 (1)	2.77 (2)	3.1942 (13)	112 (2)
N3—H1N$\cdots$N1^i	0.87 (1)	2.12 (1)	2.9337 (18)	157 (2)
N3—H2N$\cdots$N2^{ii}	0.87 (1)	2.23 (1)	3.0173 (18)	150 (2)
O1W—H1W$\cdots$O1	0.87 (1)	2.29 (2)	3.0792 (16)	151 (2)
O1W—H2W$\cdots$O2W^{iii}	0.87 (1)	1.94 (1)	2.8075 (17)	176 (2)
O2W—H3W$\cdots$N2^{iv}	0.87 (1)	2.07 (1)	2.9308 (17)	171 (2)
O2W—H4W$\cdots$O3W^v	0.87 (1)	1.94 (1)	2.8053 (13)	173 (2)
O3W—H5W$\cdots$O2^{iii}	0.88 (1)	2.58 (3)	3.1279 (10)	121 (2)
O3W—H5W$\cdots$N3^{vi}	0.88 (1)	2.32 (2)	3.0506 (16)	140 (3)

Symmetry codes: (i) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, -y+\frac{5}{2}, -z+1$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (v) $x, y-1, z$; (vi) $-x, y, -z+\frac{1}{2}$.

Table 4
Hydrogen-bond geometry (Å, °) for CsCTZ.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H1N$\cdots$O1W^i	0.88 (1)	2.00 (2)	2.864 (5)	168 (7)
N3—H2N$\cdots$N1^{ii}	0.88 (1)	2.25 (3)	3.048 (5)	151 (5)
O1W—H1W$\cdots$N2^{iii}	0.88 (1)	1.96 (3)	2.761 (5)	150 (6)
O1W—H2W$\cdots$O3^{iv}	0.88 (1)	2.05 (3)	2.867 (5)	154 (7)

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

maps for NaCTZ and KCTZ are available as supporting information. As some O—H distances of the freely refined models were slightly short (0.79 Å), the final reported models restrained X—H (X = O or N) to be 0.88 (1) Å (see Tables 2–4). Similar treatment of CsCTZ gave a structure with the same protonation behaviour for the CTZ anion as was found herein for NaCTZ and KCTZ. The H atoms of the disordered half-occupancy water molecule of NaCTZ were added in calculated positions that gave sensible intermolecular hydrogen-bonding contacts (see Table 2). Thus, electron-density data clearly gives models for both NaCTZ and KCTZ that differ from those reported as APUZER and APUZIV. We think it is clear that these structures should have been described as having intact SO$_2$NH$_2$ groups and as having been deprotonated at the heterocyclic ring.
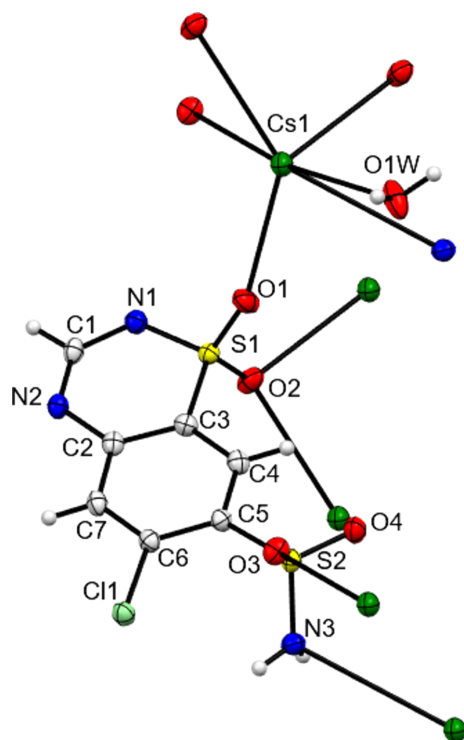
The K salt APUZOB is a mixed ethanolate/hydrate that was also reported to have a deprotonated SO$_2$NH unit (Paluch *et al.*, 2011). We were unable to obtain crystals of this form, but have investigated its deprotonation site by comparing the various bond lengths involving the N atoms of the CTZ anions. Study of Table 5 shows clear geometric differences between the salt forms that contain deprotonated CTZ anions and the neutral polymorphs of chlorothiazide (Leech *et al.*, 2008; Brydson & Kennedy, 2024). All the salt forms show similar bond lengths to each other, including the two crystallographically independent CTZ anions of APUZOB. We believe that as this group forms a coherent set, it indicates that

Figure 3
Contents of the asymmetric unit of CsCTZ, expanded so as to show all metal-to-ligand coordination bonds.
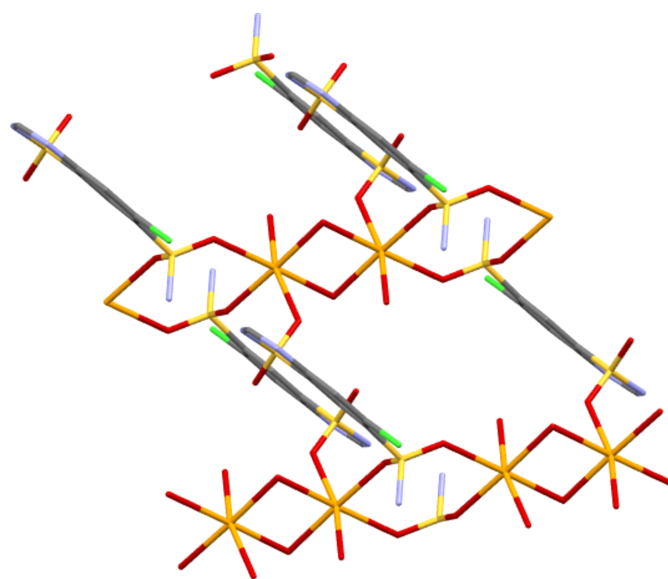

Figure 4
Detail of the coordination bonding in NaCTZ, showing one-dimensional chains with [NaONaO] and [NaOSO]$_2$ rings linked into a two-dimensional motif by CTZ anions bridging between the chains.

Table 5
Selected bond lengths (Å) for polymorphic forms 1 and 2 of CTZ, and for salt forms containing CTZ anions.

	S1—N1	N1—C1	C1—N2	N2—C2	S2—N3
CTZ, form 1	1.619	1.299	1.341	1.394	1.607
CTZ, form 2	1.620	1.309	1.344	1.391	1.590
NaCTZ	1.580 (2)	1.352 (4)	1.323 (4)	1.378 (3)	1.585 (2)
KCTZ	1.5979 (12)	1.333 (2)	1.323 (2)	1.3853 (19)	1.6086 (13)
CsCTZ	1.591 (4)	1.340 (5)	1.318 (6)	1.376 (5)	1.602 (3)
APUZOB A	1.598	1.335	1.333	1.379	1.618
APUZOB B	1.590	1.340	1.327	1.385	1.609
VEKBOF	1.577	1.333	1.306	1.385	1.599

Table 6
Bond lengths (Å) for coordination bonds in NaCTZ, KCTZ and CsCTZ.

	NaCTZ	KCTZ	CsCTZ
M—N3			3.457 (3)
M—O1	2.360 (2)	2.7813 (11)	2.952 (3)
M—O2		2.7133 (11)	3.056 (3), 3.131 (3)
M—O3	2.365 (2)	2.6720 (11)	3.162 (3)
M—O4	2.464 (2)	2.7478 (11)	
M—Cl1		3.3257 (4)	3.7738 (9)
M—OH$_2$	2.355 (2)	2.6269 (12)	3.244 (4)
	2.418 (2)	2.8493 (12)	
	2.438 (2)		

APUZOB may also have been incorrectly reported with respect to the deprotonation site, and that it should also be deprotonated at the ring N atom. Note that in the neutral polymorphs the C1—N1 bond is considerably shorter than the C2—N1 bond, indicating that it is mostly C1—N1 that has double-bond character. In contrast, for the anionic CTZ forms, C1—N1 is slightly longer than C2—N1. The chemical scheme has been drawn so as to place the double bond at the shorter C2—N1 site, but of course such small differences mean that in reality an intermediate resonance form is observed.

NaCTZ has a six-coordinate octahedral Na centre with an O$_6$ coordination set. Three of these O atoms are from water ligands (two bridging between Na centres and one terminal) and the other three are from SO$_2$ units of the CTZ anion. Details of coordination bonds for the three salt forms are given in Table 6. All three of these SO$_2$—Na bonds lead to bridges between Na centres. The SO$_2$NH$_2$ unit forms eight-membered [NaOSO]$_2$ rings which alternate with four-membered NaONaO rings (O from water) to propagate the structure perpendicular to the crystallographic b direction. The CTZ anions bridge between these chains via Na bonds to both SO$_2$ groups of CTZ to give connectivity parallel to the crystallographic a direction, giving an overall two-dimensional coordination polymer (see Fig. 4). Hydrophilic inorganic layers thus alternate with hydrophobic organic bilayers along the c direction, with the main CTZ-to-CTZ interactions across the organic bilayers being from N—H$\cdots$N hydrogen bonds (Table 2 and Fig. 5).

The K centre in KCTZ is seven-coordinate and has a somewhat unusual O$_6$Cl coordination shell. The two water ligands are terminal and thus the coordination polymer builds solely through interactions with the CTZ anions. The unbound water molecule sits on a crystallographic twofold axis, giving an overall stoichiometry of KCTZ·2.5H$_2$O. Each K centre bonds to four CTZ anions through interactions with all four chemically distinct O atoms of CTZ. There is also a relatively unusual bond to Cl of a CTZ anion. At 3.3257 (4) Å, the K—Cl bond with the organic halide is similar to, or only slightly longer than, typical bond lengths reported between K and chloride anions (*e.g.* 3.325 and 3.094 Å in ZUKDUH and BEPSAS, respectively) (Zaleskaya *et al.*, 2020; Yang *et al.*, 2013). Alkali metal to organic halide bonds are described in the literature, but most are observed with simple poly-halogenated aromatics and relatively few with less substituted rings (*e.g.* Smith, 2015; Rosokha *et al.*, 2009; Mastropierro *et*
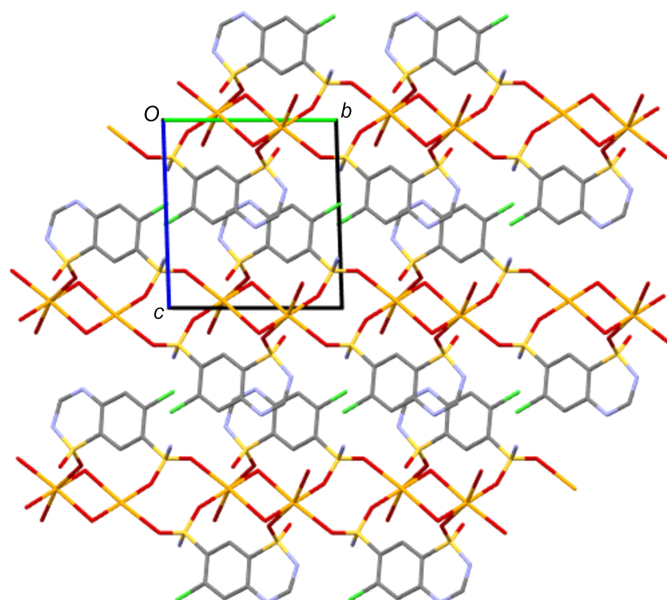
al., 2022; Osterloh *et al.*, 2001). A rare example of such a bond in a drug material is the Na—Cl bond observed in the structure of the Na salt of diclofenac (Oyama *et al.*, 2021). With each K centre making bonds with five neighbouring CTZ anions, the result is a three-dimensional coordination polymer as shown in Fig. 6. K-to-O interactions form a two-dimensional structure parallel to the crystallographic c direction and it is the K—Cl bonds that link these layers into the three-dimensional coordination polymer. These bonds in the third dimension are supported by N—H$\cdots$N hydrogen bonds and by hydrogen bonds involving both coordinated and noncoordinated water molecules. The overall packing structure displays inorganic and organic layers alternating along the crystallographic c direction (see Fig. 6).

Despite the large size of the Cs cation, CsCTZ has a Cs centre with a maximum of seven dative bonds, the same as found for K in KCTZ. These form an O$_5$NCl coordination shell. Although consistent with the treatment of KCTZ above, it is debatable whether or not the Cs—Cl contact of 3.7738 (9) Å should be considered as a dative bond, because although this distance is shorter than the sum of the van der Waals radii for the two atoms, it is longer than the sum of the

Figure 5
Packing structure of NaCTZ, viewed along the a axis and showing organic and inorganic layers alternating along the c direction.
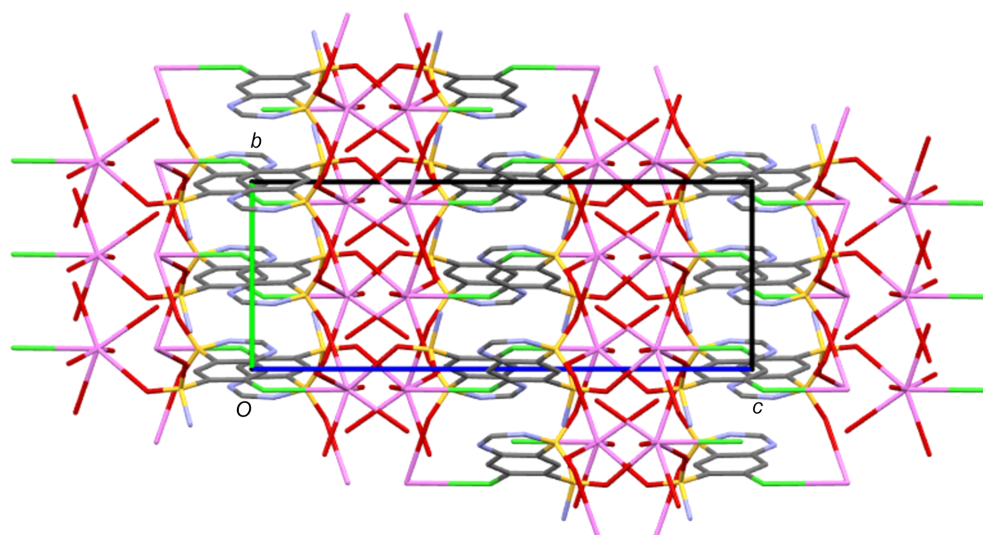
Figure 6
Packing structure of KCTZ, viewed along the a axis and showing organic and inorganic layers alternating along the c direction.

ionic radii. A search of the CSD showed that the Cs—Cl contact herein is approximately 0.2–0.4 Å longer than contacts described as Cs—Cl bonds, but that some structures do include similar distances as formal R—Cl bonds to Cl atoms (*e.g.* XELZAQ, NEPNIH and DIQZAG) (Cametti *et al.*, 2006; Smith, 2013*a*,*b*). CsCTZ is the only structure herein to form an M—N bond, and it is notable that this bond is not with a formally charge-carrying ring N atom, but is with the N3 atom of the SO_2NH_2 group. At 3.457 (3) Å, the Cs—N bond is considerably longer than the Cs—O bonds [range 2.952 (3)–3.244 (4) Å]. As with KCTZ, the sole water ligand is terminal. The other six interactions involve a Cs centre contacting six different neighbouring CTZ anions. The bonds to O and to N give a two-dimensional coordination polymer lying parallel to the crystallographic ab plane (see Fig. 7). Contacts between

these planes which would result in a three-dimensional construct are limited to the Cs—Cl interactions discussed above and to N—H$\cdots$N hydrogen bonds, with the latter motif being similar to that found in NaCTZ. Again, as in NaCTZ, a layered structure is formed with inorganic layers and organic bilayers alternating along the crystallographic c direction.

In all three structures, both ring N atoms act as hydrogen-bond acceptors (see Tables 2–4). The ring sulfonamide N atom always accepts a single hydrogen bond from a neighbouring NH_2 moiety. The closeness in space of the two N atoms of these interactions may go some way to explaining why APUZER and APUZIV incorrectly assign an H atom to the ring rather than to NH_2. In all three structures, ring atom N2 accepts a hydrogen bond from a metal-coordinated water molecule and, in the case of KCTZ only, it also accepts a second hydrogen bond from a NH_2 group. As well as the interactions described above, the NH_2 groups of NaCTZ and CsCTZ also donate hydrogen bonds to water molecules. Only in KCTZ does the NH_2 group act as a hydrogen-bond acceptor, accepting a bond from the non-metal-coordinated water molecule. The O atoms of the SO_2 groups of the CTZ anions only accept hydrogen bonds from water molecules and thus make no CTZ-to-CTZ contacts.

4. Summary

Both modelling electron density and geometric comparisons with other structures suggest that the previously reported NaCTZ and KCTZ structures APUZER and APUZIV have been misidentified both in terms of hydration state and in terms of the deprotonated site of the CTZ anion. Both should have the formula MCTZ$\cdot$2.5H$_2$O and both should feature deprotonation of the CTZ heterocyclic ring, rather than of the SO_2NH_2 group. The Cs salt CsCTZ is found to crystallize as CsCTZ$\cdot$H$_2$O and has the same deprotonation site on the CTZ heterocyclic ring as do its Na and K cognates. An unusual feature for salt structures of drug anions is that both KCTZ
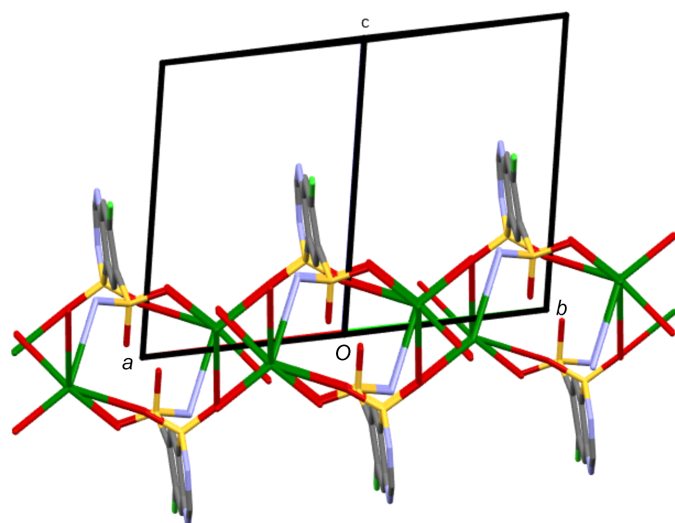

Figure 7
Part of the structure of KCTZ, showing the two-dimensional coordination motif formed by Cs—O and Cs—N bonds. Cs—Cl and hydrogen bonds link neighbouring motifs, along the c direction, into a three-dimensional network.

and CsCTZ display M—Cl contacts with the chlorobenzene group, although that in the Cs salt is relatively long. Both these structures give coordination polymers where M—O, or M—O and M—N, bonds give two-dimensional moieties. It is the M—Cl contact that expands the K and Cs coordination polymers into the third dimension. Lacking any Na—Cl contact, the structure of NaCTZ remains a two-dimensional coordination polymer.

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supporting information

On the deprotonation of chlorothiazide

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Computing details

Poly[[μ-aqua-aqua(μ_3-6-chloro-1,1-dioxo-7-sulfamoyl-2H-1,2,4-benzothiadiazin-2-ido)sodium] hemihydrate] (NaCTZ)

Crystal data

[Na(C$_7$H$_5$ClN$_3$O$_4$S$_2$)(H$_2$O)$_2$]·0.5H$_2$O	$Z = 2$
$M_r = 362.74$	$F(000) = 370$
Triclinic, $P\overline{1}$	$D_x = 1.815$ Mg m^{-3}
$a = 8.3728$ (7) Å	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$b = 9.0819$ (8) Å	Cell parameters from 9631 reflections
$c = 9.6533$ (6) Å	$\theta = 4.6$–71.1°
$\alpha = 83.013$ (6)°	$\mu = 6.16$ mm^{-1}
$\beta = 74.055$ (6)°	$T = 100$ K
$\gamma = 70.189$ (7)°	Slab cut from mass, colourless
$V = 663.70$ (10) Å^3	0.13 × 0.11 × 0.05 mm

Data collection

Rigaku Synergy-i diffractometer	2522 independent reflections
Radiation source: microsource tube	2427 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.045$
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2019)	$\theta_{max} = 71.9°$, $\theta_{min} = 5.8°$
$T_{min} = 0.587$, $T_{max} = 1.000$	$h = -10\rightarrow10$
10937 measured reflections	$k = -11\rightarrow10$
	$l = -11\rightarrow10$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.042$	
$wR(F^2) = 0.121$	$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 0.9303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	
2522 reflections	$(\Delta/\sigma)_{max} < 0.001$
210 parameters	$\Delta\rho_{max} = 0.87$ e Å^{-3}
8 restraints	$\Delta\rho_{min} = -0.45$ 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)
Na1	0.51193 (13)	0.31409 (11)	0.96262 (10)	0.0181 (2)	
Cl1	−0.21121 (8)	1.00632 (7)	0.44660 (6)	0.01987 (19)	
S1	0.20461 (8)	0.41614 (7)	0.75673 (6)	0.01702 (19)	
S2	−0.33213 (7)	0.95212 (7)	0.80244 (6)	0.01555 (19)	
O1	0.2997 (3)	0.4640 (2)	0.8388 (2)	0.0255 (4)	
O2	0.0816 (3)	0.3409 (2)	0.8458 (2)	0.0275 (5)	
O3	−0.3553 (2)	0.8628 (2)	0.93696 (19)	0.0187 (4)	
O4	−0.2981 (2)	1.0975 (2)	0.8019 (2)	0.0212 (4)	
O1W	0.3229 (2)	0.5162 (2)	1.13402 (19)	0.0193 (4)	
H1W	0.310 (4)	0.517 (4)	1.2268 (13)	0.029*	
H2W	0.2147 (19)	0.559 (4)	1.127 (3)	0.029*	
O2W	0.6943 (3)	0.2247 (2)	1.1313 (3)	0.0303 (5)	
H3W	0.699 (5)	0.309 (3)	1.161 (4)	0.045*	
H4W	0.804 (2)	0.179 (4)	1.087 (4)	0.045*	
O3W	1.0038 (7)	0.0570 (6)	0.9401 (6)	0.0455 (12)	0.5
H5W	1.029387	0.151659	0.908877	0.068*	0.5
H6W	1.055461	0.041235	0.843577	0.068*	0.5
N1	0.3385 (3)	0.3055 (3)	0.6325 (2)	0.0223 (5)	
N2	0.2754 (3)	0.4861 (3)	0.4312 (2)	0.0228 (5)	
N3	−0.4954 (3)	0.9832 (3)	0.7372 (3)	0.0212 (5)	
C1	0.3591 (4)	0.3552 (3)	0.4928 (3)	0.0248 (6)	
H1	0.449735	0.283357	0.427239	0.030*	
C2	0.1403 (3)	0.5962 (3)	0.5181 (3)	0.0175 (5)	
C3	0.0902 (3)	0.5811 (3)	0.6693 (3)	0.0157 (5)	
C4	−0.0516 (3)	0.6927 (3)	0.7517 (3)	0.0164 (5)	
H4	−0.081828	0.679362	0.853710	0.020*	
C5	−0.1487 (3)	0.8226 (3)	0.6863 (3)	0.0153 (5)	
C6	−0.0982 (3)	0.8418 (3)	0.5352 (3)	0.0159 (5)	
C7	0.0416 (3)	0.7320 (3)	0.4535 (3)	0.0183 (5)	
H7	0.072603	0.747406	0.351726	0.022*	
H1N	−0.564 (4)	0.925 (4)	0.770 (4)	0.033 (10)*	
H2N	−0.538 (5)	1.076 (2)	0.700 (4)	0.045 (11)*	

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Na1	0.0214 (5)	0.0139 (5)	0.0206 (5)	−0.0058 (4)	−0.0083 (4)	0.0017 (4)
Cl1	0.0238 (3)	0.0144 (3)	0.0211 (3)	−0.0043 (2)	−0.0096 (2)	0.0043 (2)
S1	0.0197 (3)	0.0121 (3)	0.0194 (3)	−0.0021 (2)	−0.0096 (2)	0.0009 (2)

S2	0.0164 (3)	0.0115 (3)	0.0177 (3)	−0.0030 (2)	−0.0042 (2)	−0.0006 (2)
O1	0.0300 (10)	0.0185 (9)	0.0309 (10)	−0.0015 (8)	−0.0198 (9)	−0.0023 (8)
O2	0.0266 (10)	0.0222 (10)	0.0315 (11)	−0.0076 (8)	−0.0091 (8)	0.0105 (8)
O3	0.0204 (9)	0.0157 (9)	0.0170 (9)	−0.0037 (7)	−0.0034 (7)	0.0019 (7)
O4	0.0244 (10)	0.0141 (9)	0.0245 (9)	−0.0074 (7)	−0.0027 (8)	−0.0026 (7)
O1W	0.0225 (9)	0.0181 (9)	0.0178 (9)	−0.0074 (7)	−0.0053 (7)	0.0008 (7)
O2W	0.0353 (12)	0.0223 (10)	0.0420 (12)	−0.0144 (9)	−0.0214 (10)	0.0090 (9)
O3W	0.044 (3)	0.034 (3)	0.053 (3)	−0.015 (2)	0.000 (2)	−0.002 (2)
N1	0.0261 (12)	0.0142 (10)	0.0239 (11)	−0.0008 (9)	−0.0088 (9)	−0.0008 (9)
N2	0.0249 (12)	0.0207 (11)	0.0194 (11)	−0.0029 (9)	−0.0049 (9)	−0.0028 (9)
N3	0.0185 (11)	0.0171 (11)	0.0278 (12)	−0.0043 (9)	−0.0092 (9)	0.0042 (9)
C1	0.0228 (14)	0.0222 (14)	0.0266 (14)	−0.0019 (11)	−0.0064 (11)	−0.0050 (11)
C2	0.0180 (12)	0.0159 (12)	0.0191 (12)	−0.0047 (10)	−0.0055 (10)	−0.0026 (9)
C3	0.0168 (12)	0.0131 (11)	0.0176 (12)	−0.0034 (9)	−0.0070 (9)	0.0006 (9)
C4	0.0178 (12)	0.0162 (12)	0.0163 (11)	−0.0064 (10)	−0.0051 (9)	0.0007 (9)
C5	0.0159 (12)	0.0123 (11)	0.0182 (12)	−0.0048 (9)	−0.0046 (9)	−0.0008 (9)
C6	0.0197 (12)	0.0121 (11)	0.0182 (12)	−0.0055 (9)	−0.0097 (10)	0.0033 (9)
C7	0.0219 (13)	0.0179 (12)	0.0159 (12)	−0.0069 (10)	−0.0060 (10)	0.0012 (9)

Geometric parameters (Å, º)

Na1—O1W^i	2.355 (2)	O2W—H4W	0.874 (10)
Na1—O1	2.360 (2)	O3W—O3W^{iv}	1.459 (10)
Na1—O3^{ii}	2.365 (2)	O3W—H5W	0.9497
Na1—O2W	2.418 (2)	O3W—H6W	0.9188
Na1—O1W	2.438 (2)	N1—C1	1.352 (4)
Na1—O4^{iii}	2.464 (2)	N2—C1	1.323 (4)
Na1—Na1^i	3.4671 (19)	N2—C2	1.378 (3)
Cl1—C6	1.742 (2)	N3—H1N	0.880 (10)
S1—O2	1.454 (2)	N3—H2N	0.875 (10)
S1—O1	1.4546 (19)	C1—H1	0.9500
S1—N1	1.580 (2)	C2—C3	1.407 (4)
S1—C3	1.743 (2)	C2—C7	1.414 (4)
S2—O4	1.4412 (19)	C3—C4	1.390 (4)
S2—O3	1.4470 (18)	C4—C5	1.380 (3)
S2—N3	1.585 (2)	C4—H4	0.9500
S2—C5	1.775 (2)	C5—C6	1.410 (3)
O1W—H1W	0.873 (10)	C6—C7	1.371 (4)
O1W—H2W	0.874 (10)	C7—H7	0.9500
O2W—H3W	0.868 (10)		
O1W^i—Na1—O1	89.08 (8)	Na1^i—O1W—H1W	104 (2)
O1W^i—Na1—O3^{ii}	177.80 (8)	Na1—O1W—H1W	130 (2)
O1—Na1—O3^{ii}	93.09 (8)	Na1^i—O1W—H2W	111 (2)
O1W^i—Na1—O2W	86.14 (7)	Na1—O1W—H2W	116 (2)
O1—Na1—O2W	163.79 (9)	H1W—O1W—H2W	101 (2)
O3^{ii}—Na1—O2W	91.86 (7)	Na1—O2W—H3W	105 (3)
O1W^i—Na1—O1W	87.34 (7)	Na1—O2W—H4W	111 (3)

O1—Na1—O1W	77.79 (7)	H3W—O2W—H4W	102 (2)
O3ⁱⁱ—Na1—O1W	93.45 (7)	O3Wⁱᵛ—O3W—H5W	143.5
O2W—Na1—O1W	86.51 (8)	O3Wⁱᵛ—O3W—H6W	129.6
O1Wⁱ—Na1—O4ⁱⁱⁱ	95.35 (7)	H5W—O3W—H6W	77.9
O1—Na1—O4ⁱⁱⁱ	104.61 (7)	C1—N1—S1	120.88 (19)
O3ⁱⁱ—Na1—O4ⁱⁱⁱ	83.78 (7)	C1—N2—C2	118.2 (2)
O2W—Na1—O4ⁱⁱⁱ	91.27 (8)	S2—N3—H1N	118 (3)
O1W—Na1—O4ⁱⁱⁱ	176.40 (7)	S2—N3—H2N	118 (3)
O1Wⁱ—Na1—Na1ⁱ	44.61 (5)	H1N—N3—H2N	120 (4)
O1—Na1—Na1ⁱ	80.82 (6)	N2—C1—N1	131.4 (3)
O3ⁱⁱ—Na1—Na1ⁱ	136.14 (7)	N2—C1—H1	114.3
O2W—Na1—Na1ⁱ	84.92 (6)	N1—C1—H1	114.3
O1W—Na1—Na1ⁱ	42.73 (5)	N2—C2—C3	124.1 (2)
O4ⁱⁱⁱ—Na1—Na1ⁱ	139.91 (7)	N2—C2—C7	119.0 (2)
O2—S1—O1	113.07 (12)	C3—C2—C7	116.9 (2)
O2—S1—N1	110.62 (13)	C4—C3—C2	121.8 (2)
O1—S1—N1	109.82 (12)	C4—C3—S1	118.57 (19)
O2—S1—C3	108.99 (12)	C2—C3—S1	119.58 (19)
O1—S1—C3	108.63 (11)	C5—C4—C3	120.4 (2)
N1—S1—C3	105.40 (12)	C5—C4—H4	119.8
O4—S2—O3	118.27 (11)	C3—C4—H4	119.8
O4—S2—N3	109.06 (12)	C4—C5—C6	118.7 (2)
O3—S2—N3	109.68 (12)	C4—C5—S2	116.10 (19)
O4—S2—C5	108.34 (11)	C6—C5—S2	125.19 (19)
O3—S2—C5	103.78 (11)	C7—C6—C5	121.1 (2)
N3—S2—C5	107.08 (12)	C7—C6—Cl1	117.98 (19)
S1—O1—Na1	130.84 (12)	C5—C6—Cl1	120.93 (19)
S2—O3—Na1ⁱⁱ	134.86 (11)	C6—C7—C2	121.1 (2)
S2—O4—Na1ᵛ	123.99 (11)	C6—C7—H7	119.5
Na1ⁱ—O1W—Na1	92.66 (7)	C2—C7—H7	119.5
O2—S1—O1—Na1	67.61 (19)	N1—S1—C3—C4	172.8 (2)
N1—S1—O1—Na1	−56.47 (19)	O2—S1—C3—C2	−124.4 (2)
C3—S1—O1—Na1	−171.27 (15)	O1—S1—C3—C2	112.1 (2)
O4—S2—O3—Na1ⁱⁱ	151.47 (14)	N1—S1—C3—C2	−5.6 (2)
N3—S2—O3—Na1ⁱⁱ	25.59 (19)	C2—C3—C4—C5	0.3 (4)
C5—S2—O3—Na1ⁱⁱ	−88.55 (16)	S1—C3—C4—C5	−178.08 (18)
O3—S2—O4—Na1ᵛ	−55.18 (16)	C3—C4—C5—C6	−1.7 (4)
N3—S2—O4—Na1ᵛ	71.01 (15)	C3—C4—C5—S2	177.36 (19)
C5—S2—O4—Na1ᵛ	−172.77 (12)	O4—S2—C5—C4	112.7 (2)
O2—S1—N1—C1	125.0 (2)	O3—S2—C5—C4	−13.8 (2)
O1—S1—N1—C1	−109.5 (2)	N3—S2—C5—C4	−129.79 (19)
C3—S1—N1—C1	7.3 (3)	O4—S2—C5—C6	−68.3 (2)
C2—N2—C1—N1	−0.8 (5)	O3—S2—C5—C6	165.2 (2)
S1—N1—C1—N2	−5.2 (5)	N3—S2—C5—C6	49.2 (2)
C1—N2—C2—C3	2.7 (4)	C4—C5—C6—C7	1.7 (4)
C1—N2—C2—C7	−175.7 (2)	S2—C5—C6—C7	−177.2 (2)
N2—C2—C3—C4	−177.3 (2)	C4—C5—C6—Cl1	−177.98 (18)

C7—C2—C3—C4	1.1 (4)	S2—C5—C6—Cl1	3.0 (3)
N2—C2—C3—S1	1.0 (4)	C5—C6—C7—C2	−0.3 (4)
C7—C2—C3—S1	179.48 (18)	Cl1—C6—C7—C2	179.42 (19)
O2—S1—C3—C4	54.1 (2)	N2—C2—C7—C6	177.4 (2)
O1—S1—C3—C4	−69.5 (2)	C3—C2—C7—C6	−1.1 (4)

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

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N3—H1*N*⋯O2*W*ⁱⁱ	0.88 (1)	2.02 (1)	2.888 (3)	170 (4)
N3—H2*N*⋯N1ᵛ	0.88 (1)	2.10 (1)	2.969 (3)	173 (4)
O1*W*—H1*W*⋯N2ᵛⁱ	0.87 (1)	1.91 (1)	2.778 (3)	171 (3)
O1*W*—H2*W*⋯O2ⁱⁱ	0.87 (1)	2.29 (1)	3.148 (3)	169 (3)
O2*W*—H3*W*⋯O1ⁱ	0.87 (1)	2.07 (2)	2.895 (3)	160 (4)
O2*W*—H4*W*⋯O3*W*	0.87 (1)	1.97 (2)	2.797 (6)	158 (4)
O2*W*—H4*W*⋯O3*W*ⁱᵛ	0.87 (1)	2.20 (3)	2.915 (6)	139 (3)
O3*W*—H5*W*⋯O2ᵛⁱⁱ	0.95	1.90	2.853 (5)	180
O3*W*—H6*W*⋯Cl1ᵛⁱⁱⁱ	0.92	2.76	3.683 (5)	180

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

Poly[[diaqua(*μ₄*-6-chloro-1,1-dioxo-7-sulfamoyl-2*H*-1,2,4-benzothiadiazin-2-ido)potassium] hemihydrate] (KCTZ)

Crystal data

[Na(C₇H₅ClN₃O₄S₂)(H₂O)₂]·0.5H₂O
$M_r = 378.85$
Monoclinic, *C*2/*c*
$a = 18.3139 (2)$ Å
$b = 7.3622 (1)$ Å
$c = 19.9670 (2)$ Å
$β = 99.734 (1)°$
$V = 2653.40 (5)$ Å³
$Z = 8$

$F(000) = 1544$
$D_x = 1.897$ Mg m⁻³
Cu *Kα* radiation, $λ = 1.54184$ Å
Cell parameters from 12825 reflections
$θ = 4.5–71.4°$
$μ = 8.66$ mm⁻¹
$T = 100$ K
Fragment cut from large prism, colourless
$0.16 × 0.15 × 0.05$ mm

Data collection

Rigaku Synergy-i
  diffractometer
Radiation source: microsource tube
ω scans
Absorption correction: multi-scan
  (CrysAlis PRO; Rigaku OD, 2019)
$T_{min} = 0.446$, $T_{max} = 1.000$
13919 measured reflections

2543 independent reflections
2503 reflections with $I > 2σ(I)$
$R_{int} = 0.022$
$θ_{max} = 71.5°$, $θ_{min} = 4.5°$
$h = −18→22$
$k = −9→9$
$l = −24→24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2σ(F^2)] = 0.022$
$wR(F^2) = 0.062$
$S = 1.07$

2543 reflections
215 parameters
9 restraints
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 3.9765P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.48$ e Å^{-3}

$\Delta\rho_{min} = -0.38$ e Å^{-3}

Extinction correction: SHELXL2018 (Sheldrick, 2015b),
$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00031 (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	0.11773 (2)	0.89080 (4)	0.19140 (2)	0.01083 (10)
Cl1	0.09218 (2)	1.11324 (5)	0.52250 (2)	0.01243 (11)
S1	0.36653 (2)	0.89482 (4)	0.39296 (2)	0.00840 (10)
S2	0.08021 (2)	1.10414 (5)	0.35713 (2)	0.00892 (10)
O1	0.34684 (6)	0.73265 (14)	0.35300 (5)	0.0134 (2)
O2	0.39097 (6)	1.04350 (15)	0.35474 (5)	0.0140 (2)
O3	0.10107 (6)	1.12077 (14)	0.29124 (5)	0.0132 (2)
O4	0.02550 (6)	0.97116 (15)	0.36677 (5)	0.0136 (2)
O1W	0.26295 (6)	0.90304 (17)	0.22131 (6)	0.0207 (3)
O2W	0.13816 (6)	0.66881 (16)	0.30999 (6)	0.0165 (2)
O3W	0.000000	1.5291 (2)	0.250000	0.0200 (4)
N1	0.42998 (7)	0.84845 (18)	0.45591 (6)	0.0121 (3)
N2	0.35882 (7)	0.90613 (17)	0.54540 (6)	0.0108 (3)
N3	0.04938 (7)	1.29844 (18)	0.37646 (6)	0.0113 (3)
C1	0.41800 (8)	0.8576 (2)	0.51982 (8)	0.0112 (3)
H1	0.459270	0.823160	0.552876	0.013*
C2	0.29611 (8)	0.95812 (19)	0.50058 (7)	0.0092 (3)
C3	0.29070 (8)	0.96249 (19)	0.42939 (7)	0.0088 (3)
C4	0.22545 (8)	1.01253 (19)	0.38690 (7)	0.0098 (3)
H4	0.223559	1.015385	0.339074	0.012*
C5	0.16342 (8)	1.0581 (2)	0.41429 (7)	0.0092 (3)
C6	0.16830 (8)	1.0567 (2)	0.48563 (7)	0.0094 (3)
C7	0.23287 (8)	1.0099 (2)	0.52783 (7)	0.0104 (3)
H7	0.234972	1.012309	0.575683	0.012*
H1N	0.0222 (9)	1.294 (3)	0.4080 (8)	0.019 (5)*
H2N	0.0844 (9)	1.380 (2)	0.3857 (11)	0.022 (5)*
H1W	0.2919 (11)	0.830 (3)	0.2474 (11)	0.048 (7)*
H2W	0.2934 (11)	0.988 (2)	0.2134 (12)	0.039 (7)*
H3W	0.1406 (12)	0.659 (3)	0.3537 (5)	0.035 (6)*
H4W	0.0941 (7)	0.627 (3)	0.2948 (10)	0.027 (6)*
H5W	0.0100 (16)	1.457 (3)	0.2178 (11)	0.059 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.01097 (17)	0.01121 (18)	0.01004 (17)	0.00046 (11)	0.00099 (12)	−0.00086 (10)
Cl1	0.00949 (18)	0.0185 (2)	0.01009 (18)	0.00352 (12)	0.00388 (13)	0.00040 (12)
S1	0.00761 (18)	0.00937 (19)	0.00848 (18)	0.00134 (12)	0.00213 (13)	0.00021 (12)
S2	0.00730 (18)	0.01066 (19)	0.00848 (18)	0.00115 (12)	0.00046 (13)	−0.00087 (12)
O1	0.0142 (5)	0.0130 (5)	0.0130 (5)	0.0015 (4)	0.0025 (4)	−0.0032 (4)
O2	0.0131 (5)	0.0144 (6)	0.0158 (5)	0.0009 (4)	0.0058 (4)	0.0038 (4)
O3	0.0129 (5)	0.0182 (6)	0.0084 (5)	0.0034 (4)	0.0011 (4)	−0.0008 (4)
O4	0.0090 (5)	0.0146 (5)	0.0168 (5)	−0.0017 (4)	0.0009 (4)	−0.0003 (4)
O1W	0.0130 (6)	0.0229 (7)	0.0246 (6)	−0.0012 (5)	−0.0014 (5)	0.0061 (5)
O2W	0.0159 (5)	0.0199 (6)	0.0141 (5)	−0.0008 (5)	0.0031 (4)	0.0011 (5)
O3W	0.0212 (8)	0.0248 (9)	0.0127 (8)	0.000	−0.0010 (6)	0.000
N1	0.0092 (6)	0.0153 (6)	0.0114 (6)	0.0027 (5)	0.0006 (5)	0.0002 (5)
N2	0.0095 (6)	0.0127 (6)	0.0098 (6)	0.0014 (5)	0.0004 (5)	0.0004 (5)
N3	0.0101 (6)	0.0123 (6)	0.0119 (6)	0.0021 (5)	0.0027 (5)	−0.0010 (5)
C1	0.0106 (7)	0.0103 (7)	0.0119 (7)	0.0012 (5)	−0.0005 (5)	0.0004 (5)
C2	0.0093 (7)	0.0073 (7)	0.0107 (7)	−0.0010 (5)	0.0012 (5)	−0.0001 (5)
C3	0.0085 (7)	0.0075 (7)	0.0111 (7)	−0.0003 (5)	0.0032 (5)	−0.0006 (5)
C4	0.0115 (7)	0.0092 (7)	0.0086 (6)	−0.0009 (5)	0.0017 (5)	−0.0005 (5)
C5	0.0088 (7)	0.0082 (7)	0.0100 (7)	−0.0002 (5)	−0.0001 (5)	−0.0002 (5)
C6	0.0088 (7)	0.0084 (7)	0.0120 (7)	−0.0008 (5)	0.0046 (5)	−0.0009 (5)
C7	0.0116 (7)	0.0108 (7)	0.0088 (6)	−0.0013 (6)	0.0020 (5)	−0.0004 (5)

Geometric parameters (Å, º)

K1—O1W	2.6269 (12)	O2W—H3W	0.869 (9)
K1—O3	2.6720 (11)	O2W—H4W	0.870 (9)
K1—O2^i	2.7133 (11)	O3W—H5W	0.878 (10)
K1—O4^{ii}	2.7478 (11)	O3W—H5W^{ii}	0.878 (10)
K1—O1^{iii}	2.7813 (11)	N1—C1	1.333 (2)
K1—O2W	2.8493 (12)	N2—C1	1.323 (2)
K1—Cl1^{iv}	3.3257 (4)	N2—C2	1.3853 (19)
K1—H4W	2.92 (2)	N3—H1N	0.867 (9)
Cl1—C6	1.7337 (15)	N3—H2N	0.874 (10)
S1—O1	1.4474 (11)	C1—H1	0.9500
S1—O2	1.4480 (11)	C2—C3	1.409 (2)
S1—N1	1.5979 (12)	C2—C7	1.413 (2)
S1—C3	1.7456 (14)	C3—C4	1.393 (2)
S2—O3	1.4358 (11)	C4—C5	1.383 (2)
S2—O4	1.4369 (11)	C4—H4	0.9500
S2—N3	1.6086 (13)	C5—C6	1.4121 (19)
S2—C5	1.7753 (15)	C6—C7	1.375 (2)
O1W—H1W	0.867 (10)	C7—H7	0.9500
O1W—H2W	0.870 (10)		
O1W—K1—O3	92.73 (4)	O4—S2—C5	109.02 (7)

O1W—K1—O2[i]	96.24 (4)	N3—S2—C5	108.28 (7)
O3—K1—O2[i]	147.44 (3)	S1—O1—K1[i]	150.74 (6)
O1W—K1—O4[ii]	161.11 (4)	S1—O2—K1[iii]	152.34 (6)
O3—K1—O4[ii]	87.58 (3)	S2—O3—K1	135.34 (6)
O2[i]—K1—O4[ii]	93.57 (3)	S2—O4—K1[ii]	136.68 (6)
O1W—K1—O1[iii]	76.09 (3)	K1—O1W—H1W	127.5 (16)
O3—K1—O1[iii]	74.14 (3)	K1—O1W—H2W	129.7 (15)
O2[i]—K1—O1[iii]	138.42 (3)	H1W—O1W—H2W	102.1 (17)
O4[ii]—K1—O1[iii]	85.86 (3)	K1—O2W—H3W	149.2 (16)
O1W—K1—O2W	81.09 (4)	K1—O2W—H4W	86.0 (14)
O3—K1—O2W	76.05 (3)	H3W—O2W—H4W	102.1 (16)
O2[i]—K1—O2W	74.55 (3)	H5W—O3W—H5W[ii]	105 (4)
O4[ii]—K1—O2W	117.17 (3)	C1—N1—S1	121.80 (11)
O1[iii]—K1—O2W	141.17 (3)	C1—N2—C2	117.97 (13)
O1W—K1—Cl1[iv]	101.20 (3)	S2—N3—H1N	114.3 (14)
O3—K1—Cl1[iv]	138.42 (3)	S2—N3—H2N	112.5 (14)
O2[i]—K1—Cl1[iv]	69.95 (2)	H1N—N3—H2N	111 (2)
O4[ii]—K1—Cl1[iv]	67.21 (2)	N2—C1—N1	131.43 (14)
O1[iii]—K1—Cl1[iv]	71.65 (2)	N2—C1—H1	114.3
O2W—K1—Cl1[iv]	144.47 (3)	N1—C1—H1	114.3
O1W—K1—H4W	97.3 (2)	N2—C2—C3	124.57 (13)
O3—K1—H4W	81.1 (4)	N2—C2—C7	118.03 (13)
O2[i]—K1—H4W	66.8 (4)	C3—C2—C7	117.40 (13)
O4[ii]—K1—H4W	101.4 (3)	C4—C3—C2	121.82 (13)
O1[iii]—K1—H4W	153.9 (4)	C4—C3—S1	118.87 (11)
O2W—K1—H4W	17.30 (19)	C2—C3—S1	119.27 (11)
Cl1[iv]—K1—H4W	134.3 (3)	C5—C4—C3	120.05 (13)
C6—Cl1—K1[v]	116.30 (5)	C5—C4—H4	120.0
O1—S1—O2	113.79 (6)	C3—C4—H4	120.0
O1—S1—N1	109.73 (7)	C4—C5—C6	118.76 (13)
O2—S1—N1	109.12 (7)	C4—C5—S2	117.73 (11)
O1—S1—C3	108.88 (6)	C6—C5—S2	123.44 (11)
O2—S1—C3	110.03 (7)	C7—C6—C5	121.41 (13)
N1—S1—C3	104.90 (7)	C7—C6—Cl1	118.04 (11)
O3—S2—O4	118.71 (6)	C5—C6—Cl1	120.54 (11)
O3—S2—N3	107.61 (7)	C6—C7—C2	120.52 (13)
O4—S2—N3	107.03 (7)	C6—C7—H7	119.7
O3—S2—C5	105.84 (7)	C2—C7—H7	119.7
O2—S1—O1—K1[i]	97.01 (13)	N1—S1—C3—C4	−179.97 (12)
N1—S1—O1—K1[i]	−25.57 (15)	O1—S1—C3—C2	114.92 (12)
C3—S1—O1—K1[i]	−139.87 (12)	O2—S1—C3—C2	−119.73 (12)
O1—S1—O2—K1[iii]	124.07 (13)	N1—S1—C3—C2	−2.49 (14)
N1—S1—O2—K1[iii]	−113.01 (14)	C2—C3—C4—C5	−0.6 (2)
C3—S1—O2—K1[iii]	1.58 (16)	S1—C3—C4—C5	176.81 (11)
O4—S2—O3—K1	−35.28 (11)	C3—C4—C5—C6	1.4 (2)
N3—S2—O3—K1	−156.89 (8)	C3—C4—C5—S2	−175.42 (11)
C5—S2—O3—K1	87.50 (9)	O3—S2—C5—C4	−12.18 (13)

O3—S2—O4—K1ii	−56.10 (11)	O4—S2—C5—C4	116.57 (12)
N3—S2—O4—K1ii	65.81 (10)	N3—S2—C5—C4	−127.33 (12)
C5—S2—O4—K1ii	−177.29 (8)	O3—S2—C5—C6	171.11 (12)
O1—S1—N1—C1	−114.03 (13)	O4—S2—C5—C6	−60.14 (14)
O2—S1—N1—C1	120.66 (13)	N3—S2—C5—C6	55.97 (14)
C3—S1—N1—C1	2.80 (15)	C4—C5—C6—C7	−0.5 (2)
C2—N2—C1—N1	0.1 (3)	S2—C5—C6—C7	176.13 (11)
S1—N1—C1—N2	−2.0 (2)	C4—C5—C6—Cl1	179.84 (11)
C1—N2—C2—C3	0.2 (2)	S2—C5—C6—Cl1	−3.49 (19)
C1—N2—C2—C7	179.96 (13)	K1v—Cl1—C6—C7	1.64 (14)
N2—C2—C3—C4	178.63 (14)	K1v—Cl1—C6—C5	−178.72 (10)
C7—C2—C3—C4	−1.1 (2)	C5—C6—C7—C2	−1.2 (2)
N2—C2—C3—S1	1.2 (2)	Cl1—C6—C7—C2	178.40 (11)
C7—C2—C3—S1	−178.52 (11)	N2—C2—C7—C6	−177.75 (13)
O1—S1—C3—C4	−62.56 (13)	C3—C2—C7—C6	2.0 (2)
O2—S1—C3—C4	62.78 (13)		

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

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H1N⋯Cl1	0.87 (1)	2.77 (2)	3.1942 (13)	112 (2)
N3—H1N⋯N1vi	0.87 (1)	2.12 (1)	2.9337 (18)	157 (2)
N3—H2N⋯N2vii	0.87 (1)	2.23 (1)	3.0173 (18)	150 (2)
O1W—H1W⋯O1	0.87 (1)	2.29 (2)	3.0792 (16)	151 (2)
O1W—H2W⋯O2Wiii	0.87 (1)	1.94 (1)	2.8075 (17)	176 (2)
O2W—H3W⋯N2viii	0.87 (1)	2.07 (1)	2.9308 (17)	171 (2)
O2W—H4W⋯O3Wix	0.87 (1)	1.94 (1)	2.8053 (13)	173 (2)
O3W—H5W⋯O2iii	0.88 (1)	2.58 (3)	3.1279 (10)	121 (2)
O3W—H5W⋯N3ii	0.88 (1)	2.32 (2)	3.0506 (16)	140 (3)

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

Poly[[aqua(μ₅-6-chloro-1,1-dioxo-7-sulfamoyl-2H-1,2,4-benzothiadiazin-2-ido)caesium] (CsCTZ)

Crystal data

[Cs(C₇H₅ClN₃O₄S₂)(H₂O)]
$M_r = 445.64$
Triclinic, $P\overline{1}$
$a = 7.71260\ (1)$ Å
$b = 9.05930\ (1)$ Å
$c = 10.13810\ (1)$ Å
$\alpha = 93.9760\ (1)°$
$\beta = 107.5390\ (1)°$
$\gamma = 107.8000\ (1)°$
$V = 632.84\ (1)$ Å³

$Z = 2$
$F(000) = 428$
$D_x = 2.339$ Mg m⁻³
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 14584 reflections
$\theta = 4.6–71.3°$
$\mu = 28.08$ mm⁻¹
$T = 100$ K
Block, colourless
0.24 × 0.15 × 0.12 mm

Data collection

Rigaku Synergy-i diffractometer	2436 independent reflections
Radiation source: microsource tube	2433 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.059$
Absorption correction: gaussian (CrysAlis PRO; Rigaku OD, 2019)	$\theta_{max} = 71.3°$, $\theta_{min} = 4.7°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.022$, $T_{max} = 0.247$	$k = -11 \rightarrow 11$
14718 measured reflections	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.036$	
$wR(F^2) = 0.095$	$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 0.7171P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	
2436 reflections	$(\Delta/\sigma)_{max} < 0.001$
188 parameters	$\Delta\rho_{max} = 1.75$ e Å^{-3}
5 restraints	$\Delta\rho_{min} = -1.53$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cs1	−0.19755 (3)	0.16090 (3)	0.06985 (2)	0.02257 (13)
Cl1	1.03692 (13)	0.82370 (10)	0.53756 (9)	0.0214 (2)
S2	0.81621 (13)	0.73056 (11)	0.19288 (9)	0.0183 (2)
S1	0.38932 (13)	0.17021 (10)	0.27036 (9)	0.0184 (2)
O3	0.7174 (4)	0.6319 (3)	0.0560 (3)	0.0248 (6)
O4	0.7650 (5)	0.8660 (3)	0.2229 (3)	0.0234 (6)
O2	0.4670 (5)	0.0792 (3)	0.1954 (3)	0.0271 (7)
O1	0.2130 (4)	0.1869 (4)	0.1831 (3)	0.0295 (7)
O1W	−0.2150 (6)	0.4223 (5)	−0.1322 (3)	0.0374 (9)
N3	1.0432 (5)	0.7903 (4)	0.2161 (4)	0.0218 (7)
N2	0.5892 (5)	0.3067 (4)	0.5846 (3)	0.0190 (6)
N1	0.3536 (5)	0.0923 (4)	0.4000 (4)	0.0207 (7)
C4	0.6226 (6)	0.4561 (5)	0.2559 (4)	0.0192 (8)
H4	0.563234	0.424715	0.156832	0.023*
C1	0.4529 (6)	0.1675 (5)	0.5329 (4)	0.0204 (8)
H1	0.418951	0.110381	0.601872	0.025*
C2	0.6474 (6)	0.3975 (5)	0.4920 (4)	0.0187 (7)
C6	0.8538 (6)	0.6436 (5)	0.4595 (4)	0.0183 (7)
C7	0.7948 (6)	0.5453 (5)	0.5464 (4)	0.0202 (8)
H7	0.854654	0.577644	0.645379	0.024*
C5	0.7657 (6)	0.6024 (5)	0.3117 (4)	0.0176 (7)
C3	0.5655 (6)	0.3554 (4)	0.3436 (4)	0.0182 (7)

H1N	1.089 (10)	0.717 (6)	0.199 (8)	0.06 (2)*
H2N	1.115 (7)	0.862 (5)	0.292 (4)	0.032 (14)*
H1W	−0.305 (7)	0.401 (7)	−0.215 (3)	0.048 (18)*
H2W	−0.233 (10)	0.504 (6)	−0.095 (6)	0.07 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs1	0.02216 (18)	0.02638 (18)	0.01930 (17)	0.00832 (12)	0.00680 (12)	0.00601 (11)
Cl1	0.0226 (5)	0.0186 (4)	0.0190 (4)	0.0039 (3)	0.0049 (4)	0.0022 (3)
S2	0.0207 (5)	0.0186 (4)	0.0165 (4)	0.0067 (4)	0.0070 (4)	0.0047 (3)
S1	0.0185 (5)	0.0185 (5)	0.0167 (5)	0.0046 (4)	0.0057 (4)	0.0038 (4)
O3	0.0276 (16)	0.0257 (14)	0.0185 (14)	0.0062 (13)	0.0067 (12)	0.0063 (11)
O4	0.0287 (15)	0.0198 (14)	0.0269 (15)	0.0125 (12)	0.0117 (13)	0.0083 (12)
O2	0.0316 (16)	0.0202 (14)	0.0292 (15)	0.0024 (12)	0.0180 (13)	−0.0016 (12)
O1	0.0215 (15)	0.0335 (16)	0.0266 (15)	0.0052 (13)	0.0010 (12)	0.0133 (13)
O1W	0.046 (2)	0.048 (2)	0.0215 (16)	0.0320 (18)	0.0005 (15)	0.0001 (14)
N3	0.0194 (17)	0.0221 (17)	0.0230 (17)	0.0051 (14)	0.0085 (14)	0.0025 (13)
N2	0.0225 (16)	0.0196 (15)	0.0177 (15)	0.0102 (13)	0.0067 (13)	0.0063 (12)
N1	0.0210 (16)	0.0203 (15)	0.0204 (16)	0.0071 (13)	0.0062 (13)	0.0050 (13)
C4	0.0206 (18)	0.0205 (18)	0.0186 (17)	0.0106 (16)	0.0057 (15)	0.0042 (15)
C1	0.025 (2)	0.0232 (19)	0.0175 (18)	0.0125 (16)	0.0085 (16)	0.0075 (15)
C2	0.0214 (18)	0.0207 (18)	0.0181 (18)	0.0121 (16)	0.0072 (15)	0.0048 (14)
C6	0.0187 (18)	0.0180 (17)	0.0177 (18)	0.0072 (15)	0.0051 (15)	0.0008 (14)
C7	0.0219 (19)	0.024 (2)	0.0160 (18)	0.0117 (16)	0.0048 (15)	0.0036 (15)
C5	0.0181 (18)	0.0177 (17)	0.0175 (18)	0.0072 (15)	0.0054 (14)	0.0043 (14)
C3	0.0177 (17)	0.0165 (17)	0.0203 (18)	0.0065 (14)	0.0057 (15)	0.0028 (14)

Geometric parameters (Å, º)

Cs1—O1	2.952 (3)	S1—C3	1.743 (4)
Cs1—O2^i	3.056 (3)	O1W—H1W	0.879 (10)
Cs1—O2^{ii}	3.131 (3)	O1W—H2W	0.878 (10)
Cs1—O4^{iii}	3.162 (3)	N3—H1N	0.878 (10)
Cs1—O1W	3.244 (4)	N3—H2N	0.879 (10)
Cs1—N3^{iv}	3.457 (3)	N2—C1	1.318 (6)
Cs1—Cl1^v	3.7738 (9)	N2—C2	1.376 (5)
Cs1—S1^i	3.9823 (9)	N1—C1	1.340 (5)
Cs1—Cs1^{vi}	4.4045 (4)	C4—C3	1.386 (6)
Cs1—Cs1^i	5.2201 (4)	C4—C5	1.386 (6)
Cl1—C6	1.738 (4)	C4—H4	0.9500
S2—O4	1.439 (3)	C1—H1	0.9500
S2—O3	1.442 (3)	C2—C7	1.406 (6)
S2—N3	1.602 (3)	C2—C3	1.418 (5)
S2—C5	1.775 (4)	C6—C7	1.371 (6)
S1—O1	1.440 (3)	C6—C5	1.414 (5)
S1—O2	1.452 (3)	C7—H7	0.9500
S1—N1	1.591 (4)		

O1—Cs1—O2[i]	119.37 (9)	O3—S2—C5	104.42 (18)
O1—Cs1—O2[ii]	132.81 (9)	N3—S2—C5	110.04 (18)
O2[i]—Cs1—O2[ii]	89.22 (8)	O1—S1—O2	113.5 (2)
O1—Cs1—O4[iii]	79.80 (8)	O1—S1—N1	109.56 (18)
O2[i]—Cs1—O4[iii]	85.11 (8)	O2—S1—N1	109.89 (19)
O2[ii]—Cs1—O4[iii]	65.18 (8)	O1—S1—C3	109.91 (19)
O1—Cs1—O1W	106.11 (9)	O2—S1—C3	108.19 (18)
O2[i]—Cs1—O1W	85.42 (9)	N1—S1—C3	105.52 (19)
O2[ii]—Cs1—O1W	113.37 (9)	O1—S1—Cs1[i]	75.11 (14)
O4[iii]—Cs1—O1W	170.44 (9)	O2—S1—Cs1[i]	41.72 (13)
O1—Cs1—N3[iv]	76.42 (9)	N1—S1—Cs1[i]	110.10 (13)
O2[i]—Cs1—N3[iv]	66.43 (8)	C3—S1—Cs1[i]	139.76 (14)
O2[ii]—Cs1—N3[iv]	150.07 (8)	S2—O4—Cs1[vii]	127.51 (17)
O4[iii]—Cs1—N3[iv]	125.86 (8)	S1—O2—Cs1[i]	119.85 (17)
O1W—Cs1—N3[iv]	50.48 (9)	S1—O2—Cs1[viii]	134.98 (16)
O1—Cs1—Cl1[v]	68.96 (7)	Cs1[i]—O2—Cs1[viii]	90.78 (8)
O2[i]—Cs1—Cl1[v]	137.82 (6)	S1—O1—Cs1	160.92 (19)
O2[ii]—Cs1—Cl1[v]	65.14 (6)	Cs1—O1W—H1W	122 (4)
O4[iii]—Cs1—Cl1[v]	54.33 (6)	Cs1—O1W—H2W	113 (5)
O1W—Cs1—Cl1[v]	134.54 (6)	H1W—O1W—H2W	99 (2)
N3[iv]—Cs1—Cl1[v]	144.79 (6)	S2—N3—Cs1[iv]	119.81 (17)
O1—Cs1—S1[i]	101.00 (7)	S2—N3—H1N	115 (5)
O2[i]—Cs1—S1[i]	18.43 (6)	Cs1[iv]—N3—H1N	69 (5)
O2[ii]—Cs1—S1[i]	104.31 (5)	S2—N3—H2N	114 (4)
O4[iii]—Cs1—S1[i]	82.28 (6)	Cs1[iv]—N3—H2N	115 (4)
O1W—Cs1—S1[i]	89.14 (6)	H1N—N3—H2N	116 (6)
N3[iv]—Cs1—S1[i]	56.24 (6)	C1—N2—C2	118.2 (3)
Cl1[v]—Cs1—S1[i]	136.254 (19)	C1—N1—S1	121.5 (3)
O1—Cs1—Cs1[vi]	145.42 (6)	C3—C4—C5	120.4 (4)
O2[i]—Cs1—Cs1[vi]	45.30 (6)	C3—C4—H4	119.8
O2[ii]—Cs1—Cs1[vi]	43.92 (5)	C5—C4—H4	119.8
O4[iii]—Cs1—Cs1[vi]	69.05 (6)	N2—C1—N1	131.3 (4)
O1W—Cs1—Cs1[vi]	103.09 (7)	N2—C1—H1	114.3
N3[iv]—Cs1—Cs1[vi]	109.79 (6)	N1—C1—H1	114.3
Cl1[v]—Cs1—Cs1[vi]	102.429 (16)	N2—C2—C7	118.6 (3)
S1[i]—Cs1—Cs1[vi]	61.158 (14)	N2—C2—C3	124.8 (4)
O1—Cs1—Cs1[i]	47.10 (7)	C7—C2—C3	116.6 (4)
O2[i]—Cs1—Cs1[i]	72.44 (6)	C7—C6—C5	121.4 (4)
O2[ii]—Cs1—Cs1[i]	133.40 (6)	C7—C6—Cl1	117.6 (3)
O4[iii]—Cs1—Cs1[i]	70.74 (6)	C5—C6—Cl1	120.9 (3)
O1W—Cs1—Cs1[i]	107.52 (7)	C6—C7—C2	121.3 (4)
N3[iv]—Cs1—Cs1[i]	57.41 (6)	C6—C7—H7	119.4
Cl1[v]—Cs1—Cs1[i]	100.538 (16)	C2—C7—H7	119.4
S1[i]—Cs1—Cs1[i]	54.261 (14)	C4—C5—C6	118.2 (4)
Cs1[vi]—Cs1—Cs1[i]	106.207 (8)	C4—C5—S2	117.5 (3)
C6—Cl1—Cs1[v]	107.76 (14)	C6—C5—S2	124.2 (3)
O4—S2—O3	118.76 (18)	C4—C3—C2	122.0 (4)

O4—S2—N3	107.95 (19)	C4—C3—S1	119.4 (3)
O3—S2—N3	107.30 (18)	C2—C3—S1	118.5 (3)
O4—S2—C5	108.19 (18)		
O3—S2—O4—Cs1^{vii}	−61.6 (3)	N2—C2—C7—C6	−177.5 (4)
N3—S2—O4—Cs1^{vii}	60.7 (2)	C3—C2—C7—C6	0.7 (6)
C5—S2—O4—Cs1^{vii}	179.74 (18)	C3—C4—C5—C6	1.4 (6)
O1—S1—O2—Cs1^{i}	−24.8 (2)	C3—C4—C5—S2	−174.9 (3)
N1—S1—O2—Cs1^{i}	98.2 (2)	C7—C6—C5—C4	−2.7 (6)
C3—S1—O2—Cs1^{i}	−147.02 (17)	Cl1—C6—C5—C4	179.0 (3)
O1—S1—O2—Cs1^{viii}	101.8 (3)	C7—C6—C5—S2	173.3 (3)
N1—S1—O2—Cs1^{viii}	−135.2 (2)	Cl1—C6—C5—S2	−4.9 (5)
C3—S1—O2—Cs1^{viii}	−20.5 (3)	O4—S2—C5—C4	115.0 (3)
Cs1^{i}—S1—O2—Cs1^{viii}	126.6 (3)	O3—S2—C5—C4	−12.4 (4)
O2—S1—O1—Cs1	116.3 (6)	N3—S2—C5—C4	−127.2 (3)
N1—S1—O1—Cs1	−6.9 (7)	O4—S2—C5—C6	−61.1 (4)
C3—S1—O1—Cs1	−122.4 (6)	O3—S2—C5—C6	171.5 (3)
Cs1^{i}—S1—O1—Cs1	99.5 (6)	N3—S2—C5—C6	56.7 (4)
O4—S2—N3—Cs1^{iv}	−99.20 (19)	C5—C4—C3—C2	0.9 (6)
O3—S2—N3—Cs1^{iv}	29.9 (2)	C5—C4—C3—S1	−178.5 (3)
C5—S2—N3—Cs1^{iv}	142.93 (17)	N2—C2—C3—C4	176.0 (4)
O1—S1—N1—C1	−119.3 (3)	C7—C2—C3—C4	−2.0 (6)
O2—S1—N1—C1	115.4 (3)	N2—C2—C3—S1	−4.6 (5)
C3—S1—N1—C1	−1.1 (4)	C7—C2—C3—S1	177.4 (3)
Cs1^{i}—S1—N1—C1	159.9 (3)	O1—S1—C3—C4	−59.2 (4)
C2—N2—C1—N1	−0.1 (7)	O2—S1—C3—C4	65.2 (4)
S1—N1—C1—N2	−0.5 (6)	N1—S1—C3—C4	−177.2 (3)
C1—N2—C2—C7	−179.1 (4)	Cs1^{i}—S1—C3—C4	31.1 (4)
C1—N2—C2—C3	2.9 (6)	O1—S1—C3—C2	121.4 (3)
Cs1^{v}—Cl1—C6—C7	2.6 (3)	O2—S1—C3—C2	−114.2 (3)
Cs1^{v}—Cl1—C6—C5	−179.1 (3)	N1—S1—C3—C2	3.3 (4)
C5—C6—C7—C2	1.7 (6)	Cs1^{i}—S1—C3—C2	−148.3 (2)
Cl1—C6—C7—C2	179.9 (3)		

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

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N3—H1*N*⋯O1*W*^{iv}	0.88 (1)	2.00 (2)	2.864 (5)	168 (7)
N3—H2*N*⋯N1^{vii}	0.88 (1)	2.25 (3)	3.048 (5)	151 (5)
O1*W*—H1*W*⋯N2^{ix}	0.88 (1)	1.96 (3)	2.761 (5)	150 (6)
O1*W*—H2*W*⋯O3^{ii}	0.88 (1)	2.05 (3)	2.867 (5)	154 (7)

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