



A rare positively charged nicotinic acid disulfide: 2,2'-dithiodinicotinic acid hydrochloride monohydrate

Alexander T. Chemey, Chad M. McGuire and Thomas E. Albrecht-Schmitt*

Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way Tallahassee, FL 32306, USA.

*Correspondence e-mail: albrecht-schmitt@chem.fsu.edu

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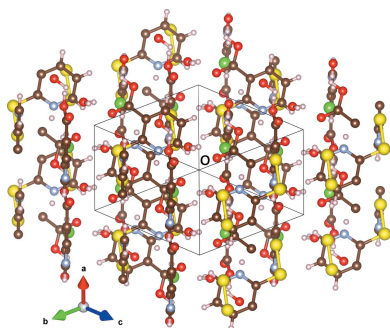
The title compound {systematic name: 3-carboxy-2-[2-(3-carboxypyridin-2-yl)disulfan-1-yl]pyridin-1-ium chloride monohydrate}, $C_{12}H_9N_2O_4S_2^+ \cdot Cl^- \cdot H_2O$, crystallizes in the triclinic space group $P\bar{1}$. A pair of 2-mercaptonicotinic acid moieties is connected by a 2,2'-disulfide bond with a dihedral angle of $78.79(3)^\circ$. One of the N atom is protonated, as are both carboxylate groups, resulting in an overall +1 charge on the dimer. The structure comprises a zigzagging layer of the dimerized dithiodinicotinic acid rings, with charge-balancing chloride ions and water molecules between the layers. Hydrogen bonding between the chloride and water sites with the dimer appears to hold the structure together. Nearest neighbor nicotinic acid rings are offset when viewed down the a axis, suggesting no added stability from ring stacking. The asymmetric unit corresponds to the empirical formula of the compound, and it packs with two formula units per unit cell.

1. Chemical context

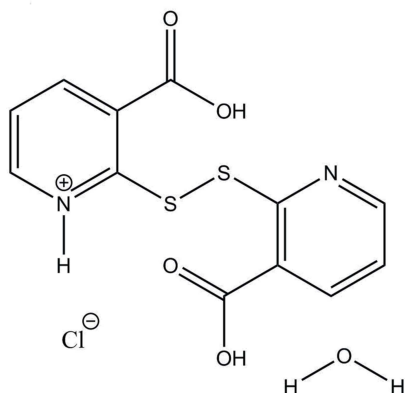
2-Mercaptonicotinic acid (2-mnaH) is commonly used as a multi-dentate ligand. It is a flexible hard/soft ligand, capable of binding *via* a carboxylate oxygen and sulfur, or nitrogen and sulfur on a single metal site. This flexibility has been exploited in a variety of reactions with hard and soft metals to produce diverse structures. Mercaptonicotinic acid complexes with silver(I) and gold(I) have proven anti-microbial properties (Nomiya *et al.*, 2000), while transition metal–mna clusters have provided fertile ground for luminescence studies (Sun *et al.*, 2011). In some extraordinary cases, all three potential binding sites of 2-mna coordinate to metal centers (Humphrey *et al.*, 2006). 2-mnaH tends to form disulfide bonds with itself in neutral solutions, and these dimers have provided interesting coordination modes with the lanthanides (Li *et al.*, 2008; Wang *et al.*, 2011), as have related 2,2'-dithiodisalicic acid compounds (Zhong *et al.*, 2014). Disulfide formation is typically inhibited by the use of acidic solution, and these non-dimerized species often feature protonated nitrogens, such as in $H Au(mnaH)_2$ (Nomiya *et al.*, 2000). It is therefore quite unusual to have a disulfide bond form from a solution acidic enough to make a nicotinium species.

2. Structural commentary

The title compound (Fig. 1), referred to as $H(2-mnaH)_2Cl \cdot H_2O$, crystallizes in the triclinic space group $P\bar{1}$. A pair of 2-mnaH moieties is connected by a 2.0491(9) Å di-



sulfide bond with a dihedral angle of $78.79(3)^\circ$. The structure features a zigzagging layer structure. The presence of a chloride in the structure mandates an overall positive charge on the dimerized species, as there is no evidence of the co-crystallized water being a hydronium ion. One nitrogen is protonated and the nicotinate ring which incorporates that charge is assigned the descriptor of α moiety. Both carboxylate groups are protonated.



3. Supramolecular features

Nicotinic acid rings are offset when viewed down the a axis with distances of $3.822(3)$ Å between nearest neighbor ring-bound atoms. This is illustrated in Fig. 2. The $\text{H}(2\text{-mnaH})_2^+$ layers stack along the c axis. Between the layers are the water molecules and chloride anions, which hold the layers together through hydrogen bonding (Table 1). These inter-layer sites are visible when viewed along $[111]$, as seen in Fig. 3. The acidic hydrogen on the α carboxylate (H4) is $1.52(3)$ Å from the co-crystallized water oxygen atom (O5), apparently pointing at a lone pair, with a total O4–O5 distance of only $2.5164(19)$ Å. This close proximity is likely the cause of the

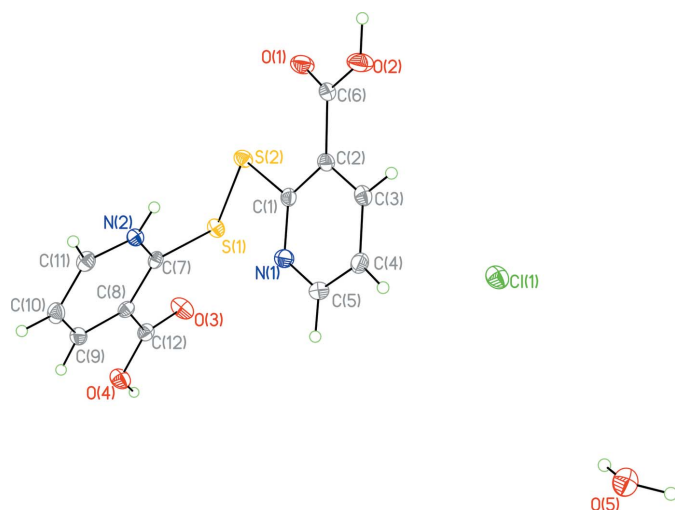


Figure 1
Displacement ellipsoid plot (50% probability level) of $\text{H}(2\text{-mnaH})_2\text{Cl}\cdot\text{H}_2\text{O}$.

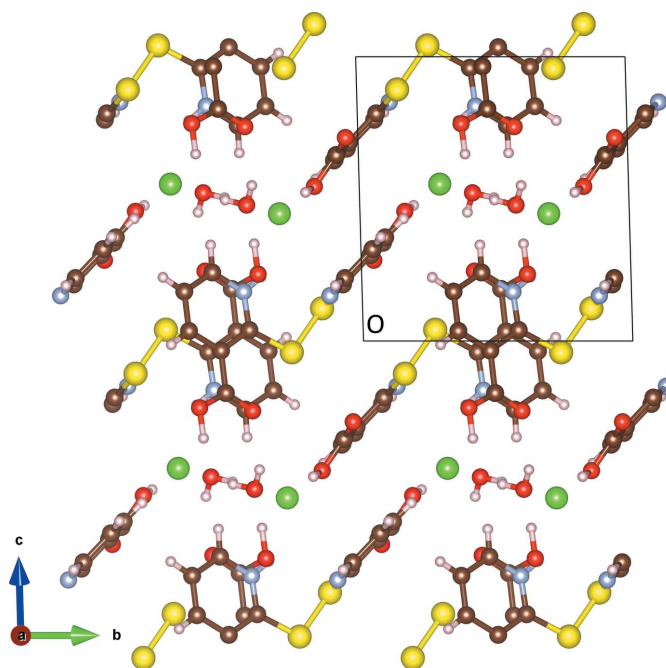


Figure 2
The packing of $\text{H}(2\text{-mnaH})_2\text{Cl}\cdot\text{H}_2\text{O}$, as viewed down the a axis. Note the zigzag shape of the layers, and the offset configuration of the nicotinic acid rings. Color code: yellow, sulfur; brown, carbon; pale blue, nitrogen; green, chlorine; pale pink, hydrogen.

long O4–H4 distance of $1.01(3)$ Å, as the hydrogen is significantly attracted to the lone pair of O5. The β moiety acidic hydrogen (H3) is pointing almost directly at the inter-layer chloride. The co-crystallized water has one hydrogen pointing towards the chloride (H2), and one hydrogen (H1) pointing approximately towards the doubly-bonded oxygen (O3) in the α moiety. The protonated nitrogen points into

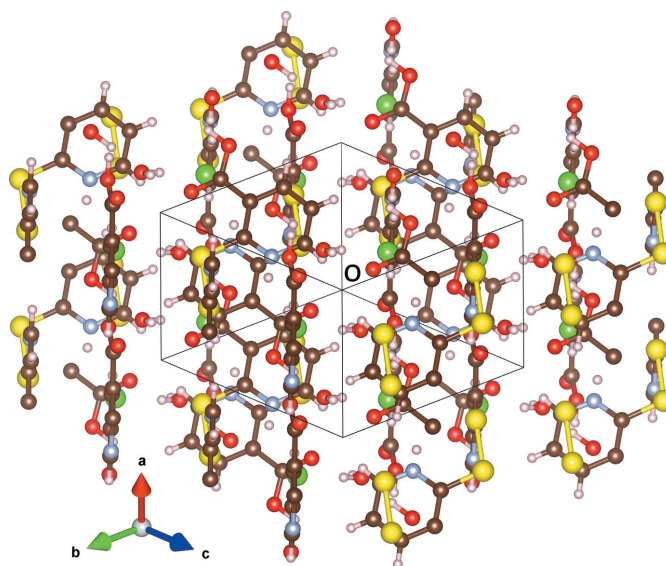


Figure 3
The view down $[111]$, illustrating the inter-layer chloride and water sites which stitch the cationic dimers together.

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

<i>D</i> — <i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i>	<i>H</i> ··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>
N2—H2A···Cl1 ⁱ	0.84 (2)	2.41 (2)	3.1228 (15)	143 (2)
C10—H10···O1 ⁱⁱ	0.91 (2)	2.53 (2)	3.405 (2)	162.0 (18)
C11—H11···Cl1 ⁱⁱⁱ	0.94 (2)	2.74 (2)	3.4776 (18)	135.7 (15)
C4—H4A···O1 ^{iv}	0.90 (2)	2.63 (2)	3.259 (2)	128.5 (17)
C4—H4A···Cl1	0.90 (2)	2.89 (2)	3.6340 (19)	141.1 (17)
O4—H4···O5 ^v	1.01 (3)	1.52 (3)	2.5164 (19)	169 (3)
O2—H3···Cl1 ^{vi}	0.91 (3)	2.12 (3)	3.0197 (15)	170 (3)
O5—H1···O3 ^{vii}	0.85 (3)	2.10 (3)	2.8709 (19)	151 (3)
O5—H2···Cl1 ^{viii}	0.88 (3)	2.20 (3)	3.0848 (16)	177 (3)

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

space between the α -connected sulfur and the chloride ion. Hydrogen bonding with the chloride anions and co-crystallized water molecules appears to dictate the staggered layered structure, but the potential for π - π interactions between parallel rings cannot be excluded.

4. Database survey

The disulfide dihedral angle of $\text{H}(2\text{-mnaH})_2\text{Cl}\cdot\text{H}_2\text{O}$ is comparable to the dihedral angles observed in 2,2'-disulfanyldisalicylic acid of 74.9 (8) and 77.7 (6)° (Humphrey & Wood, 2003), but notably smaller than the values of 88.70 (6) and 89.22 (6)° from the structure published by Rowland *et al.* (2011). In the absence of a bulky metal cation, Yehye *et al.* (2009) measured a 2,2'-dithiodinicotinate dihedral angle of 89.2 (2)°. Two different dimerized 2-mna dysprosium compounds featured dihedral angles of 84.85 (6) (Wang *et al.*, 2011), 88.77 (4) and 0.00° (Li *et al.*, 2008). The second structure is an exciting example of a lanthanide-dithiodinicotinate with two separate dimer moieties and shockingly different dihedral angles. Slightly different structures of 2,2'-disulfanyldinicotinic acid have been produced as the monohydrate (Corban *et al.*, 2012; Zhu *et al.*, 2002); these structures have dihedral angles of 87.43 (3) and 87.33 (4)°, respectively.

In situ production of the dimer has been exploited in several syntheses to make a harder ligand with binding predominantly through the carboxylic oxygens (Singh *et al.*, 2012; Li *et al.*, 2008). Similar reactivity of the sulfur site has been accomplished with 2-thiosalicylic acid to produce a simple dimer (Humphrey & Wood, 2003), while a broader study explored the products obtained with heating and variable pH (Rowland *et al.*, 2011). In that study, acidic environments prevented disulfide formation at pH even as high as 4.4, a strong contrast to the species here. Four structures have been reported to the CSD (Version 1.18; Groom *et al.*, 2016) with a protonated nitrogen on 2-mnaH, none of which featured disulfides. One structure featured sulfur sites binding to gold(I) (Nomiya *et al.*, 2000), while another was bonded through the sulfur and an oxygen site to zinc(II) (Casarin *et al.*, 2010). The other two structures were zwitterionic monomers featuring overall neutral or negative charges on the nicotinic acid moiety

(Smith & Sagatys, 2003; Kouroulis *et al.*, 2009). There is no positively charged 2-mnaH moiety currently listed in the CSD. There is also no nitrogen-protonated disulfide nicotinic species in the CSD.

In contrast to work with 2,2'-disulfanyldisalicylic acid (Humphrey & Wood, 2003; Rowland *et al.*, 2011), hydrogen bonding directly between carboxylic acid groups does not appear to play a large role. Although it is not possible to exclude the possibility that the pyridinium hydrogen atom is engaged in hydrogen bonding, as in studies of ammonium 2-mercaptopyridine-3-carboxylate hydrate (Smith & Sagatys, 2003), the location of the pyridinium in space makes this less likely.

5. Synthesis and crystallization

$\text{H}(2\text{-mnaH})_2\text{Cl}\cdot\text{H}_2\text{O}$ was grown from 23.5 mg of 2-mnaH (90+%, Alfa Aesar) with 30 mmol of 1 mol/L $\text{Ho}(\text{NO}_3)_3$ in 1 mL of a mixture of methanol and ethanol with three drops of concentrated HCl. The composition of the alcohol mixture was varied systematically from pure ethanol to pure methanol in 10% increments, and crystals were examined in an optical microscope to determine size and quality. The largest and least-occluded crystals ($\sim 0.5 \times 0.2 \times 0.2 \text{ mm}^3$ prior to cutting) were grown from a 70% ethanol/30% methanol mixture, though crystals that were smaller and diffracted weakly were grown from more methanol-rich solutions. Both methanol-rich and ethanol-rich solutions produced the same structures. The components were heated in a 7 mL vial with the lid off for twenty minutes at 325 K, though crystals similar to those grown from methanol-rich media were grown without the heating step. Comparable reactions with 1 mol L⁻¹ HoCl_3 and 1 mol L⁻¹ PrCl_3 yielded no visible crystals, while reactions with 1 mol L⁻¹ $\text{Pr}(\text{NO}_3)_3$ produced visually similar crystals that diffracted poorly. Reactions which proceeded without a lanthanide nitrate did not produce single crystals, as did all reactions without acid. It is uncertain at this time whether a metal or nitrate is necessary for these crystals to grow.

Lanthanide chlorides and nitrates were produced from heating Ho_2O_3 (Aldrich, 99.9%) and Pr_6O_{11} (Aldrich, 99.9%) in the presence of hydrochloric or nitric acid to dryness, to produce $\text{Ho}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$, $\text{HoCl}_3\cdot 6\text{H}_2\text{O}$, $\text{PrCl}_3\cdot 7\text{H}_2\text{O}$, and $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$. Stock solutions were produced after weighing out a known amount of the hydrated species and dissolving in an appropriate amount of water for the desired concentration. Reproduction experiments determined the pH with a Fisher Scientific AB15 pH Meter calibrated with pH 4, 7, and 10 buffers. The pH before acidification of a 9.2 mg/1.185 mL (0.050 mol L⁻¹) 2-mnaH solution was 4.30, and the pH after acidification with 0.150 mL of 12.1 mol L⁻¹ HCl was determined to be -0.44.

The crystals grew as large blocky yellow octahedra on the base of the vial. A large crystal was cut down to an appropriate size. Single crystals were isolated from Krytox oil with Cryo-Loops, then optically aligned on a Bruker D8 Quest X-ray diffractometer using a digital camera. Initial intensity measurements were performed using a $I\mu\text{S}$ X-ray source, a

30 W microfocused sealed tube (Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$) with high-brilliance and high-performance focusing Quazar multi-layer optics. Standard *APEX3* software was used for determination of the unit cells and data collection control. The intensities of reflections of a sphere were collected by a combination of four sets of exposures (frames). Each set had a different φ angle for the crystal and each exposure covered a range of 0.5° in ω . A total of 1464 frames were collected with an exposure time per frame of 20 s. *SAINTE* software was used for data integration including Lorentz and polarization corrections. A semi-empirical absorption correction was applied using the program *SCALE (SADABS)*.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Prospective peaks at appropriate distances from the 4, 5, and 6 carbon positions were observed on both rings and allowed to refine independently of their carbons. Hydrogen atoms were also observed as prospective peaks at distances of approximately 1 \AA from a carboxylic oxygen for both moieties, and $0.8\text{--}0.9 \text{ \AA}$ from the co-crystallized water oxygen. The command *HADD* in *SHELXP* suggested potential hydrogen atoms at reasonable distances from nitrogen sites, but refinement of the structure led to one of the atoms detaching from the structure. Free refinement of occupancy for the remaining nitrogenic hydrogen resulted in a site occupancy factor of over 80%, so occupancy was therefore fixed to 1. Bond valence sum calculations of the structure excluding carboxylic hydrogens found that two of the four oxygens were particularly distant from ideal valency; these oxygens were closest to the unaccounted peaks previously identified, and the hydrogens were therefore assigned despite their greater-than-expected distance. Attempts to refine hydrogens on the co-crystallized water and carboxylate groups with *AFIX* restraints by *SHELXL* failed to yield reasonable results. Free refinement of occupancy for the acidic hydrogens resulted in non-physical values, so site occupancy was fixed at 1. These results led to an overall dimer charge of +1, and a balanced charge state with the interlayer chloride.

PLATON (Spek, 2009) was used to check for unresolved solvent electron density, additional symmetry, and twinning.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{12}\text{H}_9\text{N}_2\text{O}_4\text{S}_2^+ \cdot \text{Cl}^- \cdot \text{H}_2\text{O}$
M_r	362.80
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	120
a, b, c (\AA)	7.9906 (12), 9.7081 (14), 10.2704 (15)
α, β, γ ($^\circ$)	86.727 (3), 73.088 (3), 73.538 (3)
V (\AA^3)	730.73 (19)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.57
Crystal size (mm)	$0.05 \times 0.05 \times 0.03$
Data collection	
Diffractometer	Bruker D8 Quest
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2015)
T_{\min}, T_{\max}	0.688, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11750, 3483, 2974
R_{int}	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})	0.658
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.075, 1.06
No. of reflections	3483
No. of parameters	243
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.34, -0.29

Computer programs: *APEX3* and *SAINTE* (Bruker, 2015), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* and *SHELXP2014* (Sheldrick, 2015), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

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supporting information

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A rare positively charged nicotinic acid disulfide: 2,2'-dithiodinic acid hydrochloride monohydrate

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINTE* (Bruker, 2015); data reduction: *SAINTE* (Bruker, 2015); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXP2014* (Sheldrick, 2015) and *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

3-Carboxy-2-[2-(3-carboxypyridin-2-yl)disulfan-1-yl]pyridin-1-ium chloride monohydrate

Crystal data

$C_{12}H_9N_2O_4S_2^+ \cdot Cl^- \cdot H_2O$

$M_r = 362.80$

Triclinic, $P\bar{1}$

$a = 7.9906$ (12) Å

$b = 9.7081$ (14) Å

$c = 10.2704$ (15) Å

$\alpha = 86.727$ (3)°

$\beta = 73.088$ (3)°

$\gamma = 73.538$ (3)°

$V = 730.73$ (19) Å³

$Z = 2$

$F(000) = 372$

$D_x = 1.649$ Mg m⁻³

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

Cell parameters from 2974 reflections

$\theta = 2.8$ – 27.9 °

$\mu = 0.57$ mm⁻¹

$T = 120$ K

Truncated column, yellow

$0.05 \times 0.05 \times 0.03$ mm

Data collection

Bruker D8 Quest
diffractometer

Radiation source: $I\mu$ s microfocused

0.5° wide /w exposures scans

Absorption correction: multi-scan
(SADABS; Bruker, 2015)

$T_{\min} = 0.688$, $T_{\max} = 0.747$

11750 measured reflections

3483 independent reflections

2974 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.9^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.075$

$S = 1.06$

3483 reflections

243 parameters

0 restraints

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.4761P]$

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

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

$\Delta\rho_{\max} = 0.34$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.55285 (6)	0.73261 (4)	-0.03978 (4)	0.01593 (10)
S2	0.34334 (6)	0.84956 (5)	0.11499 (4)	0.01655 (10)
O4	1.03798 (18)	0.38461 (14)	-0.23492 (13)	0.0231 (3)
N1	0.6456 (2)	0.88005 (16)	0.15917 (15)	0.0183 (3)
O3	0.81335 (18)	0.58125 (14)	-0.24563 (12)	0.0241 (3)
O2	0.09614 (18)	1.16658 (15)	0.45610 (14)	0.0249 (3)
C12	0.8861 (2)	0.48353 (18)	-0.18308 (17)	0.0160 (3)
N2	0.5831 (2)	0.55966 (15)	0.17321 (14)	0.0137 (3)
H2A	0.495 (3)	0.625 (3)	0.219 (2)	0.033 (6)*
O1	0.07437 (17)	1.04648 (14)	0.28410 (14)	0.0243 (3)
C9	0.8823 (2)	0.35342 (18)	0.03531 (18)	0.0164 (3)
H9A	0.987 (3)	0.286 (2)	-0.013 (2)	0.015 (5)*
C10	0.8052 (2)	0.33966 (19)	0.17376 (18)	0.0181 (4)
H10	0.854 (3)	0.263 (2)	0.220 (2)	0.022 (5)*
C11	0.6531 (2)	0.44517 (19)	0.24083 (18)	0.0169 (3)
H11	0.596 (3)	0.443 (2)	0.334 (2)	0.016 (5)*
C5	0.7374 (2)	0.93776 (19)	0.22147 (19)	0.0196 (4)
H5A	0.869 (3)	0.901 (2)	0.192 (2)	0.021 (5)*
C7	0.6516 (2)	0.57744 (17)	0.03867 (16)	0.0129 (3)
C1	0.4649 (2)	0.92968 (17)	0.19882 (17)	0.0148 (3)
C4	0.6562 (2)	1.04237 (18)	0.32312 (18)	0.0174 (3)
H4A	0.723 (3)	1.075 (2)	0.364 (2)	0.025 (6)*
C3	0.4674 (2)	1.09120 (18)	0.36465 (17)	0.0160 (3)
H3A	0.408 (3)	1.162 (2)	0.430 (2)	0.014 (5)*
C2	0.3676 (2)	1.03471 (17)	0.30221 (17)	0.0148 (3)
C8	0.8054 (2)	0.46990 (17)	-0.03376 (16)	0.0139 (3)
C6	0.1649 (2)	1.08231 (18)	0.34541 (18)	0.0168 (3)
H4	1.093 (4)	0.396 (3)	-0.336 (3)	0.058 (8)*
H3	-0.028 (4)	1.198 (3)	0.478 (3)	0.059 (9)*
O5	1.20128 (19)	1.41990 (16)	0.52156 (14)	0.0237 (3)
H1	1.173 (4)	1.400 (3)	0.453 (3)	0.064 (9)*
H2	1.232 (4)	1.501 (3)	0.504 (3)	0.062 (9)*
C11	0.68897 (6)	1.29911 (4)	0.55204 (4)	0.01899 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0192 (2)	0.0151 (2)	0.01288 (19)	-0.00254 (16)	-0.00613 (16)	0.00176 (15)
S2	0.0152 (2)	0.0167 (2)	0.0180 (2)	-0.00215 (16)	-0.00707 (16)	-0.00083 (16)

O4	0.0219 (7)	0.0223 (7)	0.0173 (6)	-0.0006 (5)	0.0010 (5)	-0.0002 (5)
N1	0.0158 (7)	0.0178 (7)	0.0211 (7)	-0.0038 (6)	-0.0052 (6)	-0.0020 (6)
O3	0.0269 (7)	0.0260 (7)	0.0130 (6)	0.0015 (6)	-0.0047 (5)	0.0003 (5)
O2	0.0154 (6)	0.0293 (7)	0.0256 (7)	-0.0027 (6)	-0.0009 (5)	-0.0087 (6)
C12	0.0173 (8)	0.0159 (8)	0.0151 (8)	-0.0060 (7)	-0.0031 (6)	-0.0028 (6)
N2	0.0143 (7)	0.0137 (7)	0.0127 (7)	-0.0034 (6)	-0.0036 (5)	-0.0006 (5)
O1	0.0157 (6)	0.0252 (7)	0.0315 (7)	-0.0023 (5)	-0.0078 (5)	-0.0064 (6)
C9	0.0159 (8)	0.0142 (8)	0.0195 (8)	-0.0039 (7)	-0.0054 (7)	-0.0012 (7)
C10	0.0217 (9)	0.0166 (8)	0.0192 (8)	-0.0072 (7)	-0.0098 (7)	0.0054 (7)
C11	0.0192 (9)	0.0192 (9)	0.0143 (8)	-0.0078 (7)	-0.0059 (7)	0.0037 (7)
C5	0.0146 (9)	0.0184 (9)	0.0257 (9)	-0.0045 (7)	-0.0055 (7)	0.0001 (7)
C7	0.0156 (8)	0.0134 (8)	0.0124 (7)	-0.0069 (6)	-0.0055 (6)	0.0008 (6)
C1	0.0163 (8)	0.0121 (8)	0.0167 (8)	-0.0049 (6)	-0.0054 (6)	0.0025 (6)
C4	0.0184 (9)	0.0156 (8)	0.0204 (9)	-0.0073 (7)	-0.0068 (7)	0.0019 (7)
C3	0.0187 (8)	0.0129 (8)	0.0153 (8)	-0.0033 (7)	-0.0044 (7)	0.0013 (6)
C2	0.0146 (8)	0.0129 (8)	0.0159 (8)	-0.0028 (6)	-0.0042 (6)	0.0035 (6)
C8	0.0144 (8)	0.0155 (8)	0.0137 (8)	-0.0066 (6)	-0.0042 (6)	-0.0008 (6)
C6	0.0148 (8)	0.0122 (8)	0.0214 (9)	-0.0027 (6)	-0.0036 (7)	0.0019 (6)
O5	0.0272 (7)	0.0252 (7)	0.0181 (7)	-0.0094 (6)	-0.0031 (5)	-0.0020 (6)
C11	0.0198 (2)	0.0182 (2)	0.0150 (2)	-0.00300 (16)	-0.00111 (16)	0.00010 (15)

Geometric parameters (Å, °)

S1—C7	1.7602 (17)	C9—C10	1.391 (2)
S1—S2	2.0491 (6)	C9—H9A	0.93 (2)
S2—C1	1.8113 (17)	C10—C11	1.374 (3)
O4—C12	1.304 (2)	C10—H10	0.91 (2)
O4—H4	1.01 (3)	C11—H11	0.94 (2)
N1—C1	1.330 (2)	C5—C4	1.377 (3)
N1—C5	1.345 (2)	C5—H5A	0.97 (2)
O3—C12	1.219 (2)	C7—C8	1.408 (2)
O2—C6	1.324 (2)	C1—C2	1.402 (2)
O2—H3	0.91 (3)	C4—C3	1.388 (2)
C12—C8	1.495 (2)	C4—H4A	0.90 (2)
N2—C11	1.348 (2)	C3—C2	1.390 (2)
N2—C7	1.351 (2)	C3—H3A	0.912 (19)
N2—H2A	0.84 (2)	C2—C6	1.489 (2)
O1—C6	1.214 (2)	O5—H1	0.85 (3)
C9—C8	1.388 (2)	O5—H2	0.88 (3)
C7—S1—S2	104.35 (6)	N2—C7—C8	117.59 (15)
C1—S2—S1	101.27 (6)	N2—C7—S1	120.27 (12)
C12—O4—H4	113.0 (16)	C8—C7—S1	122.13 (12)
C1—N1—C5	116.90 (15)	N1—C1—C2	123.81 (15)
C6—O2—H3	111.6 (18)	N1—C1—S2	116.31 (13)
O3—C12—O4	125.39 (16)	C2—C1—S2	119.85 (13)
O3—C12—C8	120.99 (15)	C5—C4—C3	118.05 (17)
O4—C12—C8	113.61 (15)	C5—C4—H4A	121.2 (14)

C11—N2—C7	123.70 (15)	C3—C4—H4A	120.7 (14)
C11—N2—H2A	117.0 (16)	C4—C3—C2	119.45 (16)
C7—N2—H2A	119.2 (16)	C4—C3—H3A	121.1 (12)
C8—C9—C10	120.68 (16)	C2—C3—H3A	119.4 (12)
C8—C9—H9A	118.4 (12)	C3—C2—C1	117.55 (15)
C10—C9—H9A	120.9 (12)	C3—C2—C6	121.11 (15)
C11—C10—C9	118.45 (16)	C1—C2—C6	121.33 (15)
C11—C10—H10	120.2 (13)	C9—C8—C7	119.36 (15)
C9—C10—H10	121.4 (13)	C9—C8—C12	120.77 (15)
N2—C11—C10	120.19 (16)	C7—C8—C12	119.86 (15)
N2—C11—H11	117.2 (12)	O1—C6—O2	124.40 (16)
C10—C11—H11	122.6 (12)	O1—C6—C2	122.64 (16)
N1—C5—C4	124.23 (16)	O2—C6—C2	112.96 (15)
N1—C5—H5A	116.2 (12)	H1—O5—H2	107 (3)
C4—C5—H5A	119.6 (12)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2A \cdots C11 ⁱ	0.84 (2)	2.41 (2)	3.1228 (15)	143 (2)
C10—H10 \cdots O1 ⁱⁱ	0.91 (2)	2.53 (2)	3.405 (2)	162.0 (18)
C11—H11 \cdots C11 ⁱⁱⁱ	0.94 (2)	2.74 (2)	3.4776 (18)	135.7 (15)
C4—H4A \cdots O1 ^{iv}	0.90 (2)	2.63 (2)	3.259 (2)	128.5 (17)
C4—H4A \cdots C11	0.90 (2)	2.89 (2)	3.6340 (19)	141.1 (17)
O4—H4 \cdots O5 ^v	1.01 (3)	1.52 (3)	2.5164 (19)	169 (3)
O2—H3 \cdots C11 ^{vi}	0.91 (3)	2.12 (3)	3.0197 (15)	170 (3)
O5—H1 \cdots O3 ^{vii}	0.85 (3)	2.10 (3)	2.8709 (19)	151 (3)
O5—H2 \cdots C11 ^{viii}	0.88 (3)	2.20 (3)	3.0848 (16)	177 (3)

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