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Crystal structure of a 1,1,2,2-tetrachloroethane-solvated hydrazinecarbothioamide compound

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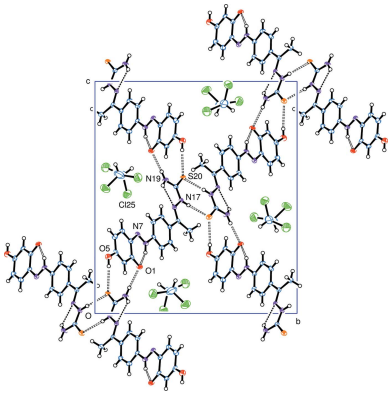
The title compound, [(1-{4-[2-(2,4-dihydroxyphenyl)diazen-1-yl]phenyl}ethylidene)amino]thiourea, 1,1,2,2-tetrachloroethane monosolvate, $C_{15}H_{15}N_5O_2S\cdot C_2H_2Cl_4$, was prepared from 4-(4-acetylphenyldiazendiyl)resorcinol and thiosemicarbazide and recrystallized from mixed solvents of tetrachloroethane and *n*-hexane. ^{1}H NMR and X-ray diffraction data are in support of the thione tautomeric form. The X-ray analysis shows the molecule crystallizes as a zwitterion, with proton transfer from the nominal phenol to the azide group; the N—N bond length is 1.291 (5) Å, and an intramolecular N—H···O hydrogen bond is formed. In the crystal, N—H···O, N—H···N and O—H···S hydrogen bonds connect the molecules into a three-dimensional network. The tetrachloroethane solvent molecules are linked to this network through weak C—H···O linkages.

1. Chemical context

Ethylidenethiosemicarbazides are polyfunctional compounds with several nucleophilic centers (NH, SH, NH_2). These compounds exist in both thione and thiol tautomeric forms, Fig. 1. 1-(1-Arylethylidene)thiosemicarbazides have been found to exhibit potent inhibitory activities against mushroom-tyrosinase (a multifunctional copper-containing enzyme that causes dermatological disorders) (Liu *et al.*, 2008, 2009). Also, 1-[1-(heterocyclic)ethylidene]thiosemicarbazides and their metal complexes have been investigated as potential anticancer agents (Finch *et al.*, 2000; Soares *et al.*, 2012; Serda *et al.*, 2012). On the other hand, ethylidenethiosemicarbazides are reactive building blocks for the construction of bioactive heterocycles, such as: [1,2,3]-thiadiazoles (El-Sadek *et al.*, 2012], imidazolinones (Thanusu *et al.*, 2010), thiazoles (Chimenti *et al.*, 2010; Abdel-Gawad *et al.*, 2010; Vazzana *et al.*, 2004; Vigato & Tamburini, 2004), and thiazolidin-4-ones (Abdel-Gawad *et al.*, 2010). It has been demonstrated that the azomethine group is accountable for biological activities shown by various types of Schiff bases (Vazzana *et al.*, 2004; Vigato & Tamburini, 2004). As part of our studies in this area, we now report the synthesis and crystal structure of the



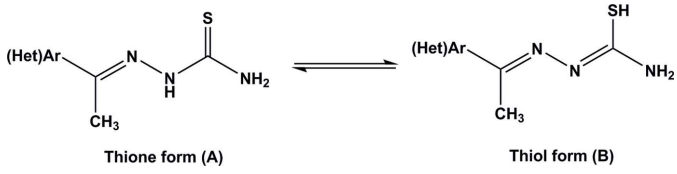


Figure 1
Tautomeric structures of ethylidenethiosemicarbazides.

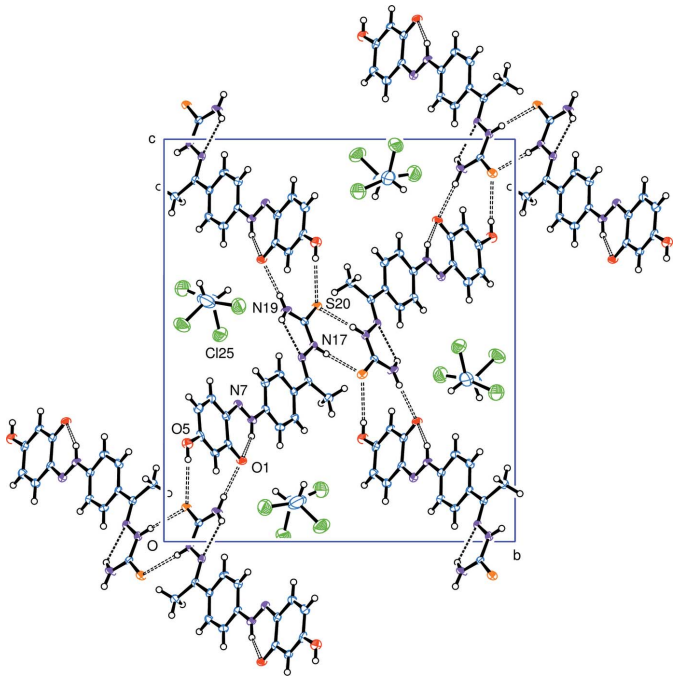


Figure 4
View of the packing in (I) along the *a*-axis direction, showing the hydrogen-bonded system.

solvated title compound, (I), containing azomethine groups and we investigate its keto and enol tautomeric forms.

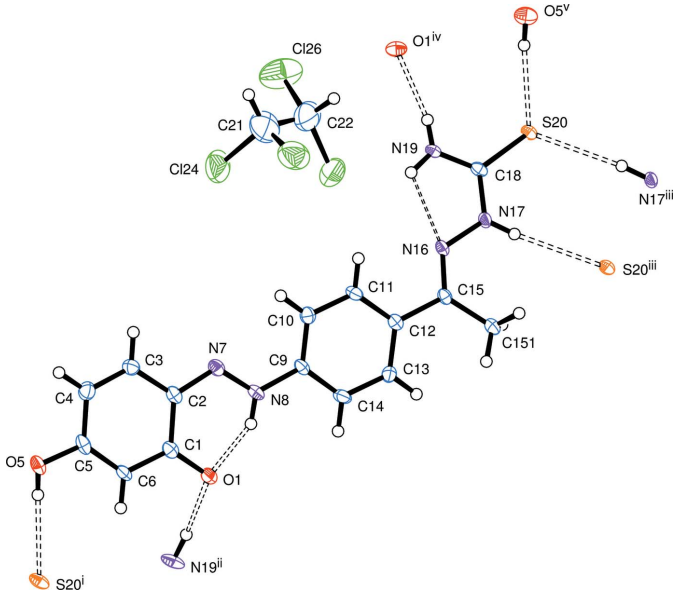
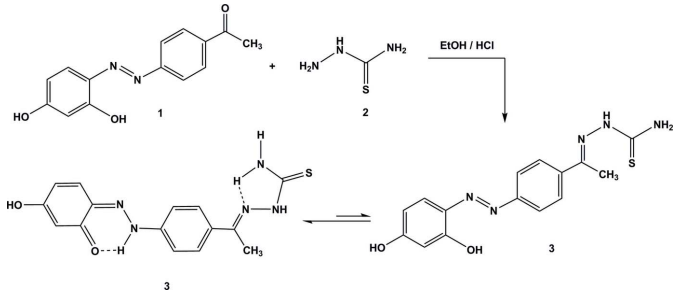


Figure 2
The molecular structure of (I) and the hydrogen-bond interactions (not including the 'weak' hydrogen bonds). Displacement ellipsoids are drawn at the 50% probability level. Symmetry operations (in the text and all figures): (i) $2+x, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x+1, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $-x-1, 1-y, 1-z$; (iv) $x-1, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x-2, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $x+1, y, z$; (vii) $-x, 1-y, 1-z$; (viii) $x-1, y, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···S20^{i}	0.93	2.89	3.634 (4)	137
C10—H10···Cl25^{ii}	0.93	2.88	3.807 (5)	172
C151—H15*C*···S20^{iii}	0.96	2.87	3.458 (4)	121
N17—H17···S20^{iii}	0.86	2.63	3.483 (4)	173
C22—H22···O1^{iv}	0.98	2.37	3.345 (8)	175
O5—H5*O*···S20^{i}	0.80 (2)	2.43 (2)	3.227 (4)	173 (5)
N8—H8*N*···O1	0.85 (2)	1.78 (3)	2.528 (4)	147 (4)
N19—H19*A*···O1^{iv}	0.84 (2)	2.05 (2)	2.862 (5)	163 (4)
N19—H19*B*···N16	0.84 (2)	2.16 (5)	2.578 (5)	111 (4)

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



2. Structural commentary

The main molecule comprises two essentially planar groups, which share the C12—C15 bond; the angle between the normals to the two planes is 13.77 (8)°, Fig. 2.

This molecule is a zwitterion, with a negative charge on O1 and a positive charge on N8: this nitrogen atom is bonded to a

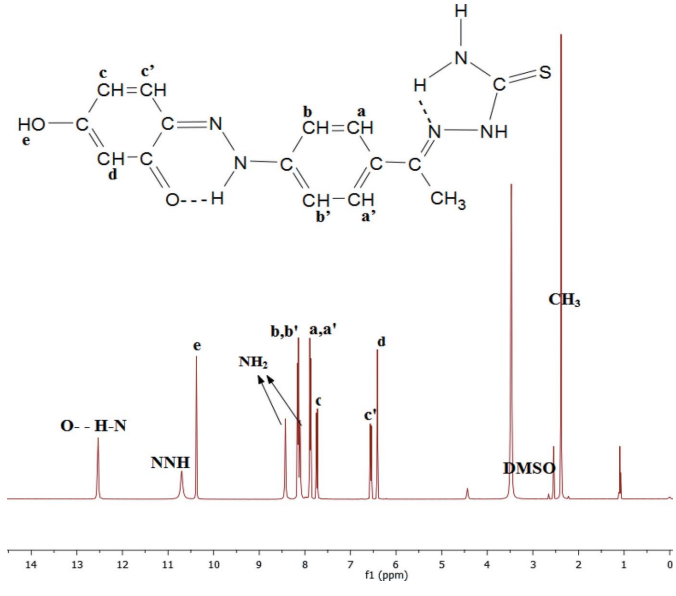


Figure 3
The ^{1}H NMR spectrum for compound **3**, showing one form of the product.

hydrogen atom (clearly identified in the X-ray analysis) and forms an intramolecular hydrogen bond N8—H8*N*···O1. There is delocalized bonding throughout the O1—C1—C2—N7—N8—C9 chain, with bond dimensions very similar to those found in a series of 1-(2-phenyldiazen-2-ium-1-yl)-naphthalen-2-olate compounds studied by Benosmane *et al.* (2013), Bougueria *et al.* (2013*a*,*b*) and Chetioui *et al.* (2013), showing a structure midway between the keto and phenolate forms of compound **3** in the Scheme; in particular, the C1—O1 bond length is 1.296 (5) Å and N7—N8 is 1.291 (5) Å.

There is a more pronounced arrangement of double and single bonds for the C═N—N group further along the molecule, with C15═N16 at 1.280 (5) Å, and N16—N17 at 1.377 (5) Å; N16 is the acceptor of a strained hydrogen bond from H19*B*.

The structure of the product was substantiated *via* spectroscopic data. For example, ^{1}H NMR spectra of compounds **3** revealed two singlet signals at δ = 2.35 and 10.28 ppm, attributed to the methyl group adjacent to hydrazone (CH_3–C═N–NH) (de Oliveira *et al.*, 2014) and NH of the hydrazone group (C═N–NH), respectively; there are also two signals (δ = 8.11 and 8.43 ppm) for the NH_2 group. A singlet signal at δ = 10.70 ppm is due to the OH group whereas the C═O···HN appears at δ = 12.53 ppm, see Fig. 3.

3. Supramolecular features

Intermolecular hydrogen bonds are shown in Table 1 and Fig. 4, and connect the molecules into a three-dimensional network. The solvent tetrachloroethane molecules are linked to this network through weak hydrogen bonds C10—H10···Cl25^{vi} and C22—H22···O1^{iv}. Other short intermolecular contacts connect molecules by π–π stacking along the *a* axis, Fig. 5; the phenyl ring of C1–C6 lies over the almost parallel ring of C9–C14 in the adjacent molecule, with C1···C14^{vi} = 3.309 Å, C3···C10^{vi} = 3.360 Å, and C5···N8^{vi} = 3.263 Å. The hydrazone group of C15···N17 is sandwiched between the C15···C18 section of an inverted molecule [with closest contacts of N17···N17^{vii} = 3.405 Å and C18···H15*C*^{vii} = 2.83Å] and the chain of N7···C11 of the stacked contact [with closest contacts N16···C10^{viii} = 3.314 Å and H15*A*···C14^{viii} = 2.93 Å].

4. Synthesis and crystallization

4-Acetylphenylazoresorcinol (Torrey & MacPherson, 1909) (**1**) (12.8 g, 50 mmol) was dissolved in 100ml of ethanol and stirred with an equimolar quantity of thiosemicarbazide (**2**) (4.55 g, 50 mmol) for 24 h at room temperature using catalytic amounts of HCl. The product, precipitated from the reaction mixture, was filtered, washed with ethanol and recrystallized from hot ethanol solution to give compound **3** as dark-red microcrystals (12.34g, 75%). Dark-red prisms of (I) were obtained by recrystallization from mixed solvents of tetrachloromethane and *n*-hexane 1:1; m.p. 521–523 K; IR (KBr): ν (cm^{-1}) 3456–3257 (OH+NH+NH_2), 1596 (C═N); ^{1}H NMR (DMSO-d_6): δ 2.35 (*s*, 3H, CH_3-C=N-NH), 6.37 (*s*, 1H, ═CH—CO), 6.56 (*d*, 1H, *J* = 4 *Hz*, ═CH—C═N), 7.69 (*d*, 1H, *J* = 4 *Hz*, ═CH—C—OH), 7.90 (*d*, 2H, *J* = 7 *Hz*, Ar-H), 8.25 (*d*, 2H, *J* = 7 *Hz*, Ar-H), 8.11 & 8.50 (2*s*, 2H, NH_2), 10.28 (*s*, 1H, NH—C═S), 10.75 (*s*, 1H, OH), 12.50 (*s*, 1H, NH—O═C) ppm; ^{13}C-NMR (DMSO-d_6): δ 13.86 CH_3—C═N—NH), 102.99 (C6), 109.33 (C3), 121.39 (C10 & C14), 127.64 (C12), 132.54 (C11 & C13), 134.35 (C2), 138.86 (C4), 146.86 (C9), 150.79 (C15), 156.64 (C5), 163.28 (C═O), 179.02 (C═S) ppm; MS *m*/*z* (%): 329 (M^+, 38), 227 (35), 171 (70), 146 (70). Analysis calculated for $C_{15}H_{15}N_5O_2S$ (329.09): C, 54.70; H, 4.59; N, 21.26; S, 9.74. Found: C, 54.61; H, 4.66; N, 21.33; S, 9.51%.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the O and N atoms were located in difference maps and were refined with distance constraints *viz* O—H distances were set to 0.82 (2) Å and N—H distances to 0.86 Å; their

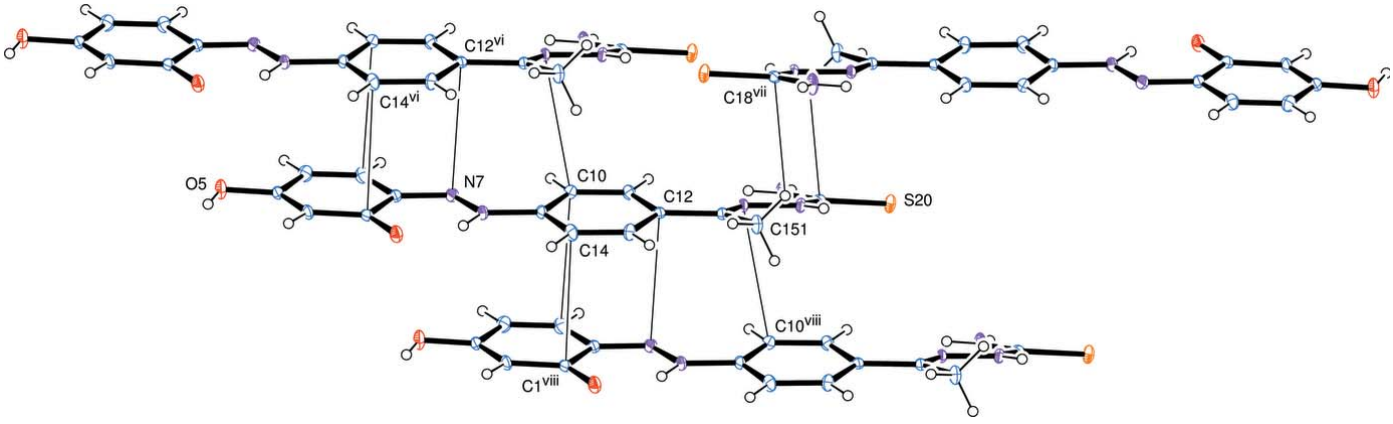


Figure 5
View of the overlapping molecules, showing some of the shorter π–π stacking contacts.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{15}N_5O_2S\cdot C_2H_2Cl_4$
M_r	497.21
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	295
a, b, c (Å)	5.9124 (2), 17.6155 (5), 20.3351 (6)
β (°)	96.563 (3)
V (Å^3)	2104.02 (11)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.69
Crystal size (mm)	0.42 × 0.09 × 0.08
Data collection	
Diffractometer	Oxford Diffraction Xcalibur 3/ Sapphire3 CCD
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.728, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28750, 3675, 3213
R_{int}	0.053
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.076, 0.204, 1.09
No. of reflections	3675
No. of parameters	279
No. of restraints	4
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.72, −0.79

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXS97* (Sheldrick, 2008), *ORTEP* (Johnson, 1976; Farrugia, 2012), *SHELXL2014* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012).

isotropic thermal parameters were refined freely. The remaining H atoms were included in idealized positions with their U_{iso} values set to ride on the U_{eq} values of the parent carbon atoms.

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supporting information

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Crystal structure of a 1,1,2,2-tetrachloroethane-solvated hydrazinecarbothioamide compound

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP* (Johnson, 1976; Farrugia, 2012); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *WinGX* (Farrugia, 2012).

[(1-{4-[2-(2,4-Dihydroxyphenyl)diazen-1-yl]phenyl}ethylidene)amino]thiourea 1,1,2,2-tetrachloroethane monosolvate

Crystal data

$C_{15}H_{15}N_5O_2S\cdot C_2H_2Cl_4$
$M_r = 497.21$
Monoclinic, $P2_1/c$
$a = 5.9124$ (2) Å
$b = 17.6155$ (5) Å
$c = 20.3351$ (6) Å
$\beta = 96.563$ (3)°
$V = 2104.02$ (11) Å^3
$Z = 4$
$F(000) = 1016$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5694 reflections
$\theta = 3.5$–$28.7°$
$\mu = 0.69$ mm^{-1}
$T = 295$ K
Prism, dark red
0.42 × 0.09 × 0.08 mm

Data collection

Oxford Diffraction Xcalibur 3/Sapphire3 CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0050 pixels mm^{-1}
Thin slice φ and ω scans
Absorption correction: multi-scan (CrysAlis PRO; Agilent, 2014)
$T_{min} = 0.728$, $T_{max} = 1.000$
28750 measured reflections
3675 independent reflections
3213 reflections with $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.6°$
$h = -7\rightarrow7$
$k = -20\rightarrow20$
$l = -24\rightarrow24$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.204$
$S = 1.09$
3675 reflections
279 parameters
4 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

$w = 1/[\sigma^2(F_o^2) + (0.0938P)^2 + 8.2654P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ 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}
O1	0.9543 (5)	0.22114 (17)	0.20187 (14)	0.0225 (7)
C1	1.0971 (7)	0.1827 (2)	0.2420 (2)	0.0183 (9)
C2	1.0684 (7)	0.1769 (2)	0.3120 (2)	0.0181 (9)
C3	1.2286 (7)	0.1342 (2)	0.3548 (2)	0.0217 (9)
H3	1.2112	0.1308	0.3996	0.026*
C4	1.4060 (7)	0.0984 (3)	0.3313 (2)	0.0239 (10)
H4	1.5092	0.0706	0.3596	0.029*
C5	1.4325 (7)	0.1039 (2)	0.2629 (2)	0.0203 (9)
O5	1.6154 (5)	0.06701 (19)	0.24376 (17)	0.0270 (7)
C6	1.2855 (7)	0.1452 (2)	0.2200 (2)	0.0187 (9)
H6	1.3101	0.1486	0.1757	0.022*
N7	0.8994 (6)	0.2111 (2)	0.34044 (17)	0.0189 (8)
N8	0.7553 (6)	0.2510 (2)	0.30244 (17)	0.0184 (8)
C9	0.5772 (7)	0.2898 (2)	0.3284 (2)	0.0170 (8)
C10	0.5488 (7)	0.2886 (2)	0.3949 (2)	0.0189 (9)
H10	0.6486	0.2612	0.4246	0.023*
C11	0.3698 (7)	0.3286 (2)	0.4168 (2)	0.0194 (9)
H11	0.3503	0.3277	0.4615	0.023*
C12	0.2182 (7)	0.3702 (2)	0.3729 (2)	0.0159 (8)
C13	0.2511 (7)	0.3713 (2)	0.3063 (2)	0.0205 (9)
H13	0.1541	0.3996	0.2765	0.025*
C14	0.4281 (7)	0.3304 (3)	0.2839 (2)	0.0221 (9)
H14	0.4468	0.3303	0.2391	0.027*
C15	0.0244 (7)	0.4110 (2)	0.3983 (2)	0.0158 (8)
C151	−0.1144 (7)	0.4677 (3)	0.3562 (2)	0.0235 (10)
H15A	−0.2643	0.4477	0.3439	0.035*
H15B	−0.0428	0.4779	0.3171	0.035*
H15C	−0.1251	0.5139	0.3807	0.035*
N16	−0.0111 (5)	0.39265 (19)	0.45721 (17)	0.0156 (7)
N17	−0.1850 (5)	0.42611 (19)	0.48636 (17)	0.0165 (7)
H17	−0.2660	0.4619	0.4670	0.020*
C18	−0.2233 (7)	0.4003 (2)	0.5467 (2)	0.0166 (9)
N19	−0.0835 (7)	0.3482 (2)	0.57381 (19)	0.0249 (9)
S20	−0.44392 (18)	0.43497 (6)	0.58404 (5)	0.0214 (3)
C21	0.2745 (18)	0.1205 (5)	0.5978 (4)	0.091 (3)
H21	0.3296	0.1016	0.6421	0.109*

C22	0.0344 (16)	0.1387 (4)	0.5960 (4)	0.076 (2)
H22	0.0155	0.1820	0.6251	0.091*
Cl23	0.4115 (4)	0.21230 (11)	0.58528 (10)	0.0710 (6)
Cl24	0.3333 (5)	0.05129 (12)	0.53859 (10)	0.0888 (8)
Cl25	−0.0877 (4)	0.16005 (11)	0.51483 (9)	0.0729 (6)
Cl26	−0.0903 (5)	0.05355 (12)	0.62934 (11)	0.0894 (8)
H5O	1.612 (8)	0.068 (3)	0.2043 (10)	0.019 (13)*
H8N	0.776 (8)	0.249 (3)	0.2620 (11)	0.021 (12)*
H19A	−0.101 (7)	0.330 (2)	0.6111 (13)	0.006 (10)*
H19B	0.023 (6)	0.336 (3)	0.552 (2)	0.025 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0237 (16)	0.0269 (17)	0.0174 (15)	0.0069 (13)	0.0040 (12)	−0.0021 (13)
C1	0.018 (2)	0.016 (2)	0.021 (2)	−0.0031 (16)	0.0043 (17)	−0.0043 (17)
C2	0.016 (2)	0.016 (2)	0.023 (2)	−0.0029 (16)	0.0061 (16)	−0.0041 (17)
C3	0.024 (2)	0.022 (2)	0.021 (2)	0.0003 (17)	0.0072 (18)	0.0012 (17)
C4	0.022 (2)	0.024 (2)	0.026 (2)	0.0029 (18)	0.0021 (18)	0.0023 (18)
C5	0.016 (2)	0.016 (2)	0.029 (2)	−0.0015 (16)	0.0068 (17)	−0.0071 (18)
O5	0.0237 (16)	0.0311 (18)	0.0277 (19)	0.0112 (14)	0.0090 (14)	−0.0021 (15)
C6	0.020 (2)	0.019 (2)	0.018 (2)	0.0012 (17)	0.0079 (17)	−0.0043 (17)
N7	0.0172 (17)	0.0191 (18)	0.0212 (18)	−0.0015 (14)	0.0056 (14)	−0.0021 (15)
N8	0.0173 (18)	0.0221 (19)	0.0167 (19)	0.0001 (14)	0.0065 (14)	−0.0041 (15)
C9	0.0158 (19)	0.017 (2)	0.020 (2)	−0.0013 (16)	0.0074 (16)	−0.0032 (16)
C10	0.017 (2)	0.019 (2)	0.021 (2)	0.0003 (16)	0.0023 (16)	−0.0008 (17)
C11	0.020 (2)	0.024 (2)	0.015 (2)	0.0007 (17)	0.0057 (16)	−0.0029 (17)
C12	0.0152 (19)	0.013 (2)	0.020 (2)	−0.0036 (15)	0.0046 (16)	−0.0029 (16)
C13	0.020 (2)	0.020 (2)	0.022 (2)	0.0050 (17)	0.0049 (17)	0.0043 (17)
C14	0.026 (2)	0.025 (2)	0.017 (2)	0.0006 (18)	0.0104 (18)	−0.0005 (17)
C15	0.0140 (19)	0.014 (2)	0.020 (2)	−0.0013 (15)	0.0043 (16)	−0.0029 (16)
C151	0.024 (2)	0.025 (2)	0.024 (2)	0.0067 (18)	0.0113 (18)	0.0018 (18)
N16	0.0137 (16)	0.0143 (17)	0.0198 (18)	0.0004 (13)	0.0061 (13)	−0.0023 (14)
N17	0.0137 (16)	0.0159 (17)	0.0205 (18)	0.0026 (13)	0.0054 (13)	0.0006 (14)
C18	0.017 (2)	0.016 (2)	0.017 (2)	−0.0047 (16)	0.0062 (16)	−0.0034 (16)
N19	0.028 (2)	0.031 (2)	0.019 (2)	0.0117 (17)	0.0143 (16)	0.0073 (16)
S20	0.0186 (5)	0.0267 (6)	0.0208 (6)	0.0054 (4)	0.0112 (4)	0.0042 (4)
C21	0.134 (8)	0.088 (6)	0.049 (4)	0.040 (6)	−0.003 (5)	−0.025 (4)
C22	0.122 (7)	0.052 (4)	0.053 (4)	0.027 (4)	0.004 (4)	−0.005 (3)
Cl23	0.0926 (14)	0.0562 (11)	0.0691 (12)	−0.0062 (10)	0.0310 (10)	−0.0010 (9)
Cl24	0.136 (2)	0.0733 (13)	0.0533 (11)	0.0549 (13)	−0.0076 (11)	−0.0175 (9)
Cl25	0.1051 (15)	0.0583 (11)	0.0539 (10)	0.0306 (10)	0.0031 (10)	0.0093 (8)
Cl26	0.136 (2)	0.0649 (13)	0.0658 (13)	−0.0453 (13)	0.0050 (12)	0.0031 (10)

Geometric parameters (Å, º)

O1—C1	1.296 (5)	C12—C15	1.494 (5)
C1—C6	1.412 (6)	C13—C14	1.389 (6)

C1—C2	1.456 (6)	C13—H13	0.9300
C2—N7	1.351 (5)	C14—H14	0.9300
C2—C3	1.426 (6)	C15—N16	1.280 (5)
C3—C4	1.356 (6)	C15—C151	1.499 (6)
C3—H3	0.9300	C151—H15A	0.9600
C4—C5	1.420 (6)	C151—H15B	0.9600
C4—H4	0.9300	C151—H15C	0.9600
C5—O5	1.356 (5)	N16—N17	1.377 (5)
C5—C6	1.369 (6)	N17—C18	1.352 (5)
O5—H5O	0.801 (19)	N17—H17	0.8600
C6—H6	0.9300	C18—N19	1.314 (6)
N7—N8	1.291 (5)	C18—S20	1.696 (4)
N8—C9	1.408 (5)	N19—H19A	0.841 (19)
N8—H8N	0.846 (19)	N19—H19B	0.84 (2)
C9—C10	1.381 (6)	C21—C22	1.451 (13)
C9—C14	1.388 (6)	C21—Cl24	1.776 (8)
C10—C11	1.387 (6)	C21—Cl23	1.840 (11)
C10—H10	0.9300	C21—H21	0.9800
C11—C12	1.398 (6)	C22—Cl25	1.766 (8)
C11—H11	0.9300	C22—Cl26	1.834 (9)
C12—C13	1.392 (6)	C22—H22	0.9800

O1—C1—C6	121.7 (4)	C14—C13—H13	119.8
O1—C1—C2	120.8 (4)	C12—C13—H13	119.8
C6—C1—C2	117.5 (4)	C9—C14—C13	120.0 (4)
N7—C2—C3	116.5 (4)	C9—C14—H14	120.0
N7—C2—C1	124.2 (4)	C13—C14—H14	120.0
C3—C2—C1	119.3 (4)	N16—C15—C12	114.6 (4)
C4—C3—C2	121.1 (4)	N16—C15—C151	124.4 (4)
C4—C3—H3	119.4	C12—C15—C151	121.0 (4)
C2—C3—H3	119.4	C15—C151—H15A	109.5
C3—C4—C5	119.3 (4)	C15—C151—H15B	109.5
C3—C4—H4	120.3	H15A—C151—H15B	109.5
C5—C4—H4	120.3	C15—C151—H15C	109.5
O5—C5—C6	122.7 (4)	H15A—C151—H15C	109.5
O5—C5—C4	115.4 (4)	H15B—C151—H15C	109.5
C6—C5—C4	121.8 (4)	C15—N16—N17	120.3 (3)
C5—O5—H5O	110 (4)	C18—N17—N16	117.3 (3)
C5—C6—C1	120.9 (4)	C18—N17—H17	121.4
C5—C6—H6	119.6	N16—N17—H17	121.4
C1—C6—H6	119.6	N19—C18—N17	116.9 (4)
N8—N7—C2	117.1 (4)	N19—C18—S20	122.9 (3)
N7—N8—C9	120.7 (3)	N17—C18—S20	120.2 (3)
N7—N8—H8N	114 (3)	C18—N19—H19A	121 (3)
C9—N8—H8N	125 (3)	C18—N19—H19B	116 (3)
C10—C9—C14	120.5 (4)	H19A—N19—H19B	124 (5)
C10—C9—N8	122.7 (4)	C22—C21—Cl24	113.7 (6)
C14—C9—N8	116.9 (4)	C22—C21—Cl23	104.3 (6)

C9—C10—C11	119.3 (4)	Cl24—C21—Cl23	112.7 (5)
C9—C10—H10	120.4	C22—C21—H21	108.7
C11—C10—H10	120.4	Cl24—C21—H21	108.7
C10—C11—C12	121.2 (4)	Cl23—C21—H21	108.7
C10—C11—H11	119.4	C21—C22—Cl25	111.4 (6)
C12—C11—H11	119.4	C21—C22—Cl26	104.1 (6)
C13—C12—C11	118.6 (4)	Cl25—C22—Cl26	112.4 (5)
C13—C12—C15	121.9 (4)	C21—C22—H22	109.6
C11—C12—C15	119.5 (4)	Cl25—C22—H22	109.6
C14—C13—C12	120.4 (4)	Cl26—C22—H22	109.6

O1—C1—C2—N7	−1.3 (6)	C10—C11—C12—C13	−0.5 (6)
C6—C1—C2—N7	178.5 (4)	C10—C11—C12—C15	178.5 (4)
O1—C1—C2—C3	180.0 (4)	C11—C12—C13—C14	1.5 (6)
C6—C1—C2—C3	−0.2 (6)	C15—C12—C13—C14	−177.6 (4)
N7—C2—C3—C4	−179.3 (4)	C10—C9—C14—C13	1.1 (6)
C1—C2—C3—C4	−0.5 (6)	N8—C9—C14—C13	−178.7 (4)
C2—C3—C4—C5	0.2 (7)	C12—C13—C14—C9	−1.7 (6)
C3—C4—C5—O5	179.5 (4)	C13—C12—C15—N16	166.6 (4)
C3—C4—C5—C6	0.9 (7)	C11—C12—C15—N16	−12.5 (5)
O5—C5—C6—C1	180.0 (4)	C13—C12—C15—C151	−12.8 (6)
C4—C5—C6—C1	−1.6 (6)	C11—C12—C15—C151	168.2 (4)
O1—C1—C6—C5	−178.9 (4)	C12—C15—N16—N17	−179.9 (3)
C2—C1—C6—C5	1.2 (6)	C151—C15—N16—N17	−0.6 (6)
C3—C2—N7—N8	178.9 (4)	C15—N16—N17—C18	175.4 (4)
C1—C2—N7—N8	0.2 (6)	N16—N17—C18—N19	3.4 (5)
C2—N7—N8—C9	−178.6 (4)	N16—N17—C18—S20	−176.5 (3)
N7—N8—C9—C10	1.1 (6)	Cl24—C21—C22—Cl25	−50.4 (9)
N7—N8—C9—C14	−179.1 (4)	Cl23—C21—C22—Cl25	72.7 (6)
C14—C9—C10—C11	−0.1 (6)	Cl24—C21—C22—Cl26	71.0 (7)
N8—C9—C10—C11	179.6 (4)	Cl23—C21—C22—Cl26	−165.9 (4)
C9—C10—C11—C12	−0.1 (6)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6···S20^{i}	0.93	2.89	3.634 (4)	137
C10—H10···Cl25^{ii}	0.93	2.88	3.807 (5)	172
C151—H15*C*···S20^{iii}	0.96	2.87	3.458 (4)	121
N17—H17···S20^{iii}	0.86	2.63	3.483 (4)	173
C22—H22···O1^{iv}	0.98	2.37	3.345 (8)	175
O5—H5*O*···S20^{i}	0.80 (2)	2.43 (2)	3.227 (4)	173 (5)
N8—H8*N*···O1	0.85 (2)	1.78 (3)	2.528 (4)	147 (4)
N19—H19*A*···O1^{iv}	0.84 (2)	2.05 (2)	2.862 (5)	163 (4)
N19—H19*B*···N16	0.84 (2)	2.16 (5)	2.578 (5)	111 (4)

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