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Andrzej Okuniewski, Jaroslaw Chojnacki, Katarzyna Baranowska and Barbara Becker

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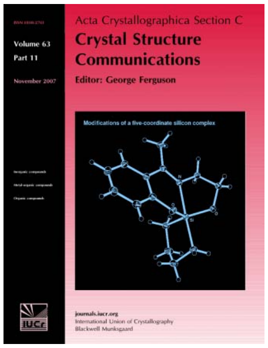

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Bis(diisopropylammonium) thiosulfate and bis(*tert*-butylammonium) thiosulfate

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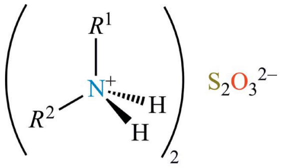
Two new dialkylammonium thiosulfates, namely bis(diisopropylammonium) thiosulfate, $2C_6H_{16}N^+\cdot S_2O_3^{2-}$, (I), and bis(*tert*-butylammonium) thiosulfate, $2C_4H_{12}N^+\cdot S_2O_3^{2-}$, (II), have been characterized. The secondary ammonium salt (I) crystallizes with $Z = 4$, while the primary ammonium salt (II), with more hydrogen-bond donors, crystallizes with $Z = 8$ and a noncrystallographic centre of inversion. In both salts, the organic cations and thiosulfate anions are linked within extensive N—H···O and N—H···S hydrogen-bond networks, forming extended two-dimensional layers. Layers are parallel to $(10\overline{1})$ in (I) and to (002) in (II), and have a polar interior and a nonpolar hydrocarbon exterior. The layered structure and hydrogen-bond motifs observed in (I) and (II) are similar to those in related ammonium sulfates.

Comment

A few years ago, we began a detailed examination of N—H···S hydrogen bonds and have prepared and structurally characterized several alkylammonium thiolate adducts (Baranowska *et al.*, 2003, 2006). We found that the hydrogen bonds in these adducts were of a robust charge-assisted N^+–H···S^- type and because of the proton transfer they are better described as salts (Becker *et al.*, 2004). We turned our attention to the thiosulfate anion because it can act as an *S*-donor ligand (Pladzyk *et al.*, 2012) and, besides oxygen, one of its S atoms is able to serve as a hydrogen-bond acceptor.

Thiosulfates belong to the basic type of inorganic anion. In most applications, salts with alkali metal cations or NH_4^+ are used as solids or in aqueous solution. By replacement of the cation with an organic species, $[R_nNH_{4-n}]^+$ (n = 1–4), we expected to obtain new substances with enhanced solubility and increased reactivity in non-aqueous phases. The chemical and physical properties of such salts, as well as their crystal structures, are rarely reported. Although a recent search of the Cambridge Structural Database (CSD, Version 5.33, August 2012; Allen, 2002) gives over 100 records containing the $S_2O_3^{2-}$ anion, there are only six alkylammonium thiosulfates, mainly obtained by chance during studies focused on other targets. Two of those papers deal with protonated cryptands (Maubert *et al.*, 2001; Nelson *et al.*, 2004) and two more are tetraalkylammonium derivatives (Leyten *et al.*, 1988; Yang & Ng, 2011). The most relevant reports are papers containing structural details of thiosulfate derivatives of piperazine (Srinivasan *et al.*, 2011) and amantadine (Jiang *et al.*, 1998).

In this study, we investigated two new members of this interesting class of salts, namely bis(diisopropylammonium) thiosulfate, $(iPr_2NH_2)_2S_2O_3$, (I) (Fig. 1), and bis(*tert*-butylammonium) thiosulfate, $(t\text{-}BuNH_3)_2S_2O_3$, (II) (Fig. 2).



(I) $R^1 = R^2 =$ iPr
(II) $R^1 = t$-Bu, $R^2 =$ H

The asymmetric unit of (I) contains two $iPr_2NH_2^+$ cations and one $S_2O_3^{2-}$ anion (Fig. 1) connected through four types of charge-assisted hydrogen bonds. Two of these hydrogen bonds, *viz.* N1—H1*M*···O1^{i} and N1—H1N···O3 (see Table 1 for details of the hydrogen bonds and symmetry codes), form a strong $R_4^4(12)$ motif (denoted **A**; Fig. 3) about an inversion centre (Etter, 1990). Larger centrosymmetric $R_{12}^{12}(36)$ rings (denoted **B**), incorporating six positive and six negative ions, are also formed by using both the N1—H and N2—H donors (Fig. 3).

It is noteworthy that four $t\text{-}BuNH_3^+$ cations and two $S_2O_3^{2-}$ anions form the asymmetric unit of (II) (Fig. 2). A noncrystallographic centre of inversion lies at about ($\frac{1}{2}$, 0.39, $\frac{1}{4}$). The ions in (II) are connected by 12 types of charge-assisted hydrogen bonds, forming a complex network. Hydrogen bonds form a strong $R_4^2(8)$ structural motif (denoted **C**; Fig. 4) and several larger rings, *viz.* $R_4^3(10)$ (denoted **D** and **D′**; based on OO+O acceptors), $R_4^4(12)$ (denoted **E**, **F** and **F′**; **E** is based on OS+OS and both **F** and **F′** on OO+OS acceptor atoms). Motifs **C** and **E** have the noncrystallographic centres of inversion at

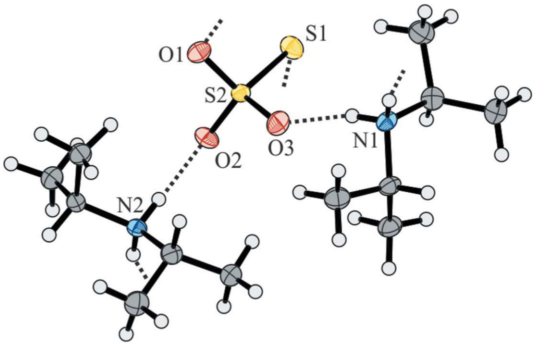


Figure 1
The structure of (I), with displacement ellipsoids drawn at the 50% probability level. Selected hydrogen bonds are marked with dotted lines.

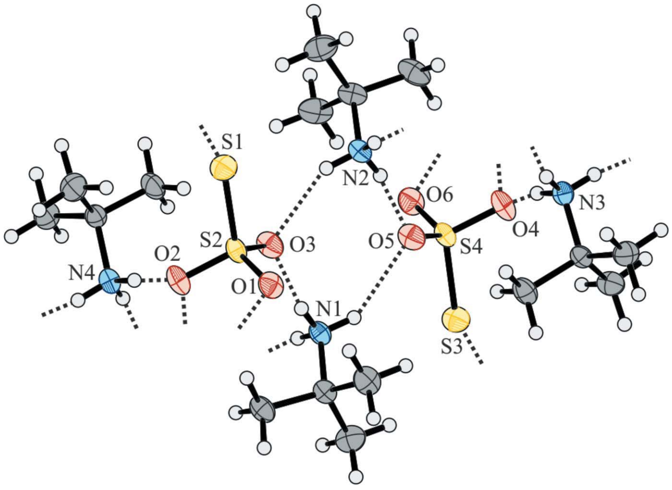


Figure 2
The structure of (II), with displacement ellipsoids drawn at the 50% probability level. Selected hydrogen bonds are marked with dotted lines.

their centres. Motifs **D**′ and **F**′ are related to **D** and **F** also by these inversions. [For more details on hydrogen bonds and symmetry codes in (II), see Table 2.]

Although there are some differences in their hydrogen bonding, both title salts crystallize in space group $P2_1/n$ and exhibit a similar layered type of structure. Each layer has a hydrophilic interior (where heteroatoms and hydrogen bonds are located) and a hydrophobic exterior (*tert*-butyl or isopropyl groups). These layers are parallel to the ($10\overline{1}$) plane in (I) and to the (002) plane in (II). Van der Waals interactions of the external alkyl groups combine these layers into three-dimensional structures (Fig. 5).

As with (II), the structure of amantadinium thiosulfate (Jiang *et al.*, 1998) has layers parallel to (002) and is characterized by the motifs $R_4^3(10)$ (based on OO+O or OS+O acceptors) and $R_4^4(12)$ (OO+OS acceptors). However, the smallest motif analogous to **C** = $R_4^2(8)$ is absent in that structure.

It is worthwhile comparing the structures of (I) and (II) to related sulfates. The structure of bis(diisopropylammonium) sulfate (Reiss & Engel, 2004) also has a layered structure

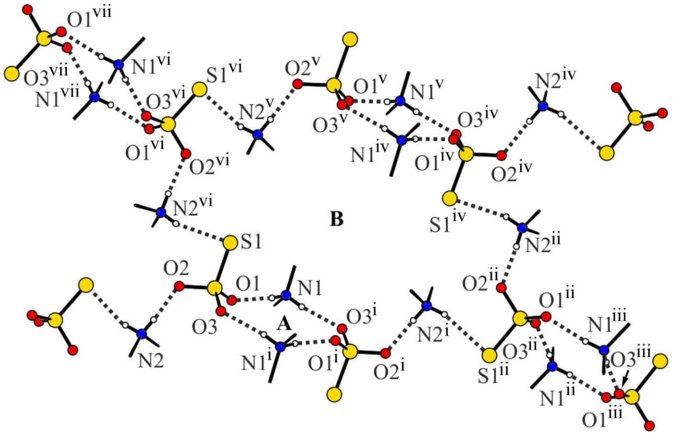


Figure 3
The hydrogen-bond pattern and ring motifs in (I). Isopropyl groups are reduced to their first C atom for clarity. Motifs: **A** = $R_4^4(12)$ and **B** = $R_{12}^{12}(36)$. [Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z-\frac{1}{2}$; (iv) $-x+1, -y+2, -z$; (v) $x, y+1, z$; (vi) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vii) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.]

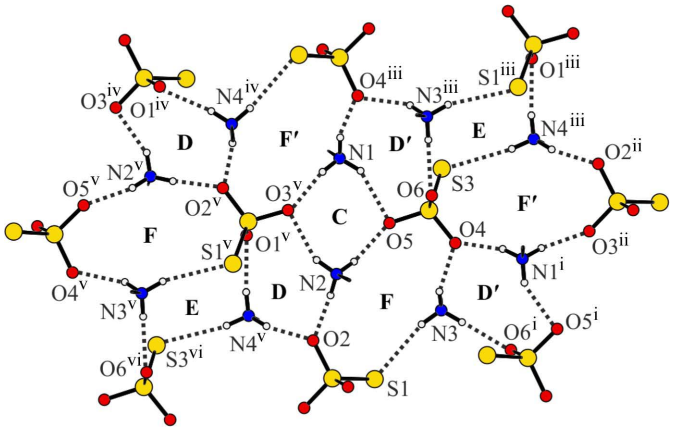
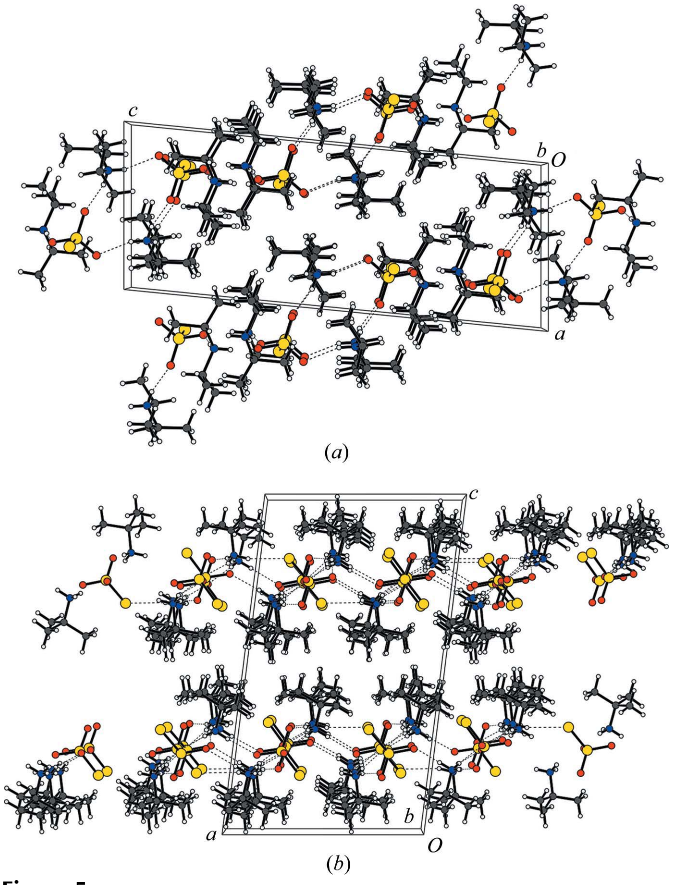


Figure 4
Selected structural ring motifs involving thiosulfate anions in (II). *tert*-Butyl groups are reduced to their first C atom for clarity. Motifs: **C** = $R_4^2(8)$, **D** = **D**′ = $R_4^3(10)$ and **E** = **F** = **F**′ = $R_4^4(12)$. [Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+1, y, z$; (iii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, y-1, z$; (v) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x-1, y, z$.]



(*a*)

(*b*)

Figure 5
Packing diagrams viewed along the [010] directions. Layers present in (*a*) (I) and (*b*) (II) are parallel to ($10\overline{1}$) and (002), respectively. Selected hydrogen bonds are marked with dotted lines.

parallel to $(10\overline{1})$ and has layers with $R_4^4(12)$ motifs and large $R_{12}^{12}(36)$ motifs, both of which are centrosymmetric. The structure of tris(diisopropylammonium) bisulfate sulfate, $(iPr_2NH_2)_3H(SO_4)_2$ (Mohammadnezhad *et al.*, 2008), is of the three-dimensional type.

Bis(*tert*-butylammonium) sulfate (Guerfel *et al.*, 2000) crystallizes in space group *C*2/*c*, exhibits a layered structure parallel to (002) and has $R_4^4(12)$ and $R_4^3(10)$ motifs within the layer, obviously based on O-atom acceptors. In this case, the asymmetric unit contains a protonated amine and half of the anion.

It is noteworthy that the structures of (I) and (II) do not contain water. This is a positive indicator for good solubility in organic phases. This should also enhance the hydrolytic stability of the substances during storage. In two protonated azacryptate hosts, which encapsulate thiosulfate anion guests, water serves as an additional hydrogen-bond donor and the perchlorate anion as a hydrogen-bond acceptor (Maubert *et al.*, 2001; Nelson *et al.*, 2004). Water is also an integral component of the hydrogen-bond network in piperazinediium thiosulfate monohydrate (Srinivasan *et al.*, 2011). Quarternary thiosulfates are hydrated also. Bis(tetraethylammonium) thiosulfate dihydrate (Leyten *et al.*, 1988) and bis(tetramethylammonium) thiosulfate tetrahydrate (Yang & Ng, 2011), being devoid of N—H bonds, exhibit a different organization based on O—H···O hydrogen bonds. The case of bis(amantadinium) thiosulfate (Jiang *et al.*, 1998), with *R* = 9.37%, is the only report in which an $–NH_3^+$ group is the sole hydrogen-bond donor and no water was found in the crystal.

Experimental

Alkylammonium thiosulfates can be obtained by different methods. Often an amine is heated with a sulfur or sulfur-containing compound. Elemental sulfur S_8 was used in the synthesis of (I), while tri-*tert*-pentoxysilanethiol [$(t\text{-AmO})_3SiSH$; Piękoś & Wojnowski, 1962] served as a source of sulfur during the preparation of (II).

For the preparation of (I), diisopropylamine (1.5 ml, 11 mmol) was mixed with elemental sulfur (0.48 g, 15 mmol) in toluene (5 ml) and the mixture was refluxed for 1.5 h. The resulting dark-brown liquid was poured into hot methanol (20 ml), filtered and the filtrate left to cool and evaporate slowly. After one week, large colourless crystals had formed. After recrystallization from a small amount of methanol, crystals suitable for single-crystal X-ray diffraction analysis were obtained.

For the preparation of (II), *tert*-butylamine (0.2 ml, 2 mmol) was added to a solution of $(t\text{-AmO})_3SiSH$ (0.65 g, 2 mmol) in toluene (5 ml) and the mixture was heated at *ca* 373 K for several hours and then left for one week at room temperature, after which time small transparent crystals had precipitated. After recrystallization from hot toluene, crystals suitable for single-crystal X-ray diffraction analysis were obtained.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*M*···O1^{i}	0.84 (1)	1.95 (1)	2.764 (2)	161 (2)
N1—H1N···O3	0.85 (1)	1.94 (1)	2.774 (2)	165 (2)
N2—H2N···O2	0.85 (1)	1.88 (1)	2.737 (2)	178 (2)
N2—H2*M*···S1^{ii}	0.85 (1)	2.55 (1)	3.3688 (17)	164 (2)

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

Salt (I)

Crystal data

$2C_6H_{16}N^+\cdot S_2O_3^{2-}$
$M_r = 316.52$
Monoclinic, $P2_1/n$
$a = 8.6437$ (3) Å
$b = 9.5322$ (3) Å
$c = 21.8594$ (8) Å
$\beta = 95.657$ (3)°
$V = 1792.30$ (11) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 120$ K
0.42 × 0.38 × 0.31 mm

Data collection

Oxford Diffraction Xcalibur (Sapphire2, large Be window) diffractometer
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.909$, $T_{max} = 0.928$
18736 measured reflections
3162 independent reflections
2858 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 1.09$
3162 reflections
196 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Salt (II)

Crystal data

$2C_4H_{12}N^+\cdot S_2O_3^{2-}$
$M_r = 260.41$
Monoclinic, $P2_1/n$
$a = 11.7834$ (4) Å
$b = 12.3519$ (6) Å
$c = 19.9312$ (8) Å
$\beta = 97.017$ (4)°
$V = 2879.2$ (2) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.36$ mm^{-1}
$T = 120$ K
0.54 × 0.12 × 0.03 mm

Data collection

Oxford Diffraction Xcalibur (Sapphire2, large Be window) diffractometer
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)]
$T_{min} = 0.834$, $T_{max} = 0.986$
10821 measured reflections
5063 independent reflections
3704 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 0.96$
5063 reflections
331 parameters
12 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

H atoms were placed at calculated positions (C–H = 0.98–0.99 Å) and treated as riding on their parent atoms, with U_{iso}(H) values set at 1.2–1.5 times U_{eq}(C). The N—H distances were restrained to 0.850 (10) Å.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1M···O4^{i}	0.85 (1)	1.96 (1)	2.797 (2)	170 (2)
N1—H1N···O3	0.85 (1)	1.99 (1)	2.833 (2)	171 (2)
N1—H1O···O5	0.85 (1)	2.19 (1)	2.934 (2)	147 (2)
N2—H2M···O3	0.86 (1)	2.09 (1)	2.876 (2)	150 (2)
N2—H2N···O2^{ii}	0.85 (1)	1.95 (1)	2.796 (2)	172 (2)
N2—H2O···O5	0.85 (1)	1.99 (1)	2.832 (2)	168 (2)
N3—H3M···O4	0.85 (1)	1.99 (1)	2.821 (2)	164 (2)
N3—H3N···O6^{iii}	0.85 (1)	1.95 (1)	2.797 (2)	172 (2)
N3—H3O···S1^{ii}	0.86 (1)	2.55 (1)	3.3491 (17)	156 (2)
N4—H4M···O1^{iv}	0.86 (1)	2.00 (1)	2.837 (2)	167 (2)
N4—H4N···O2	0.85 (1)	2.03 (1)	2.851 (2)	163 (2)
N4—H4O···S3^{i}	0.85 (1)	2.56 (1)	3.3737 (17)	160 (2)

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

For both salts, data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DT3017). Services for accessing these data are described at the back of the journal.

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supplementary materials

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Bis(diisopropylammonium) thiosulfate and bis(*tert*-butylammonium) thiosulfate

Andrzej Okuniewski, Jaroslaw Chojnacki, Katarzyna Baranowska and Barbara Becker

(I) Bis(diisopropylammonium) thiosulfate

Crystal data

$2C_6H_{16}N^+\cdot S_2O_3^{2-}$
$M_r = 316.52$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.6437$ (3) Å
$b = 9.5322$ (3) Å
$c = 21.8594$ (8) Å
$\beta = 95.657$ (3)°
$V = 1792.30$ (11) Å^3
$Z = 4$
$F(000) = 696$
$D_x = 1.173$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 13303 reflections
$\theta = 2.3$–28.8°
$\mu = 0.30$ mm^{-1}
$T = 120$ K
Prism, colourless
0.42 × 0.38 × 0.31 mm

Data collection

Oxford Diffraction Xcalibur (Sapphire2, large Be window) diffractometer
Graphite monochromator
Detector resolution: 8.1883 pixels mm^{-1}
ω scans
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)]
$T_{\min} = 0.909$, $T_{\max} = 0.928$
18736 measured reflections
3162 independent reflections
2858 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 25.0°$, $\theta_{\min} = 2.3°$
$h = -10\rightarrow10$
$k = -11\rightarrow11$
$l = -25\rightarrow25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 1.09$
3162 reflections
196 parameters
4 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 1.5638P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
H2N	0.720 (3)	0.2172 (13)	0.2016 (10)	0.022 (6)*
H1N	0.3868 (16)	0.549 (2)	0.0570 (10)	0.024 (6)*
H2M	0.702 (3)	0.126 (3)	0.2500 (5)	0.027 (6)*
H1M	0.284 (3)	0.580 (3)	0.0068 (5)	0.028 (6)*
N1	0.2993 (2)	0.58701 (19)	0.04535 (8)	0.0201 (4)
C1	0.3108 (2)	0.7406 (2)	0.06148 (10)	0.0253 (5)
H1	0.3425	0.7492	0.1066	0.03*
C2	0.4372 (3)	0.8038 (3)	0.02708 (11)	0.0320 (5)
H2A	0.5362	0.7572	0.0397	0.048*
H2B	0.4464	0.9042	0.0365	0.048*
H2C	0.4108	0.7911	−0.0172	0.048*
C3	0.1558 (3)	0.8140 (3)	0.04718 (11)	0.0328 (5)
H3A	0.1678	0.9142	0.0565	0.049*
H3B	0.0793	0.7733	0.0723	0.049*
H3C	0.12	0.8018	0.0035	0.049*
C4	0.1767 (2)	0.5011 (2)	0.07229 (10)	0.0231 (5)
H4	0.072	0.5353	0.0551	0.028*
C5	0.1959 (3)	0.3502 (2)	0.05232 (11)	0.0293 (5)
H5A	0.298	0.3153	0.0692	0.044*
H5B	0.1881	0.3455	0.0073	0.044*
H5C	0.1142	0.2923	0.0675	0.044*
C6	0.1896 (3)	0.5158 (3)	0.14167 (10)	0.0283 (5)
H6A	0.2948	0.4903	0.1588	0.042*
H6B	0.1141	0.4536	0.1585	0.042*
H6C	0.1681	0.6132	0.1525	0.042*
N2	0.69938 (19)	0.13311 (18)	0.21137 (8)	0.0187 (4)
C7	0.8243 (2)	0.0405 (2)	0.19015 (9)	0.0219 (4)
H7	0.8045	−0.0587	0.2021	0.026*
C8	0.8241 (3)	0.0488 (2)	0.12061 (10)	0.0299 (5)
H8A	0.7286	0.0063	0.101	0.045*
H8B	0.9144	−0.0017	0.108	0.045*
H8C	0.8292	0.1473	0.1081	0.045*
C9	0.9778 (3)	0.0894 (2)	0.22363 (11)	0.0297 (5)
H9A	1.0616	0.0268	0.2136	0.045*
H9B	0.9705	0.0878	0.2681	0.045*
H9C	1	0.1852	0.2108	0.045*
C10	0.5346 (2)	0.1093 (2)	0.18428 (9)	0.0227 (4)

H10	0.5287	0.1265	0.139	0.027*
C11	0.4830 (3)	−0.0403 (2)	0.19489 (11)	0.0290 (5)
H11A	0.5469	−0.1053	0.1734	0.043*
H11B	0.3736	−0.0512	0.1791	0.043*
H11C	0.4952	−0.0608	0.239	0.043*
C12	0.4342 (3)	0.2171 (2)	0.21261 (11)	0.0291 (5)
H12A	0.4407	0.2029	0.2572	0.044*
H12B	0.326	0.2065	0.1951	0.044*
H12C	0.4709	0.3116	0.2038	0.044*
S1	0.78107 (7)	0.67817 (6)	0.13521 (2)	0.02641 (17)
S2	0.72833 (5)	0.47611 (5)	0.12360 (2)	0.01745 (15)
O1	0.81990 (17)	0.41513 (16)	0.07674 (6)	0.0250 (3)
O2	0.76781 (18)	0.40428 (15)	0.18289 (6)	0.0249 (3)
O3	0.56176 (17)	0.45898 (17)	0.10376 (7)	0.0296 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0169 (9)	0.0279 (10)	0.0153 (9)	0.0010 (7)	0.0012 (7)	−0.0014 (7)
C1	0.0279 (11)	0.0270 (11)	0.0206 (10)	−0.0001 (9)	0.0006 (8)	−0.0033 (9)
C2	0.0264 (12)	0.0342 (13)	0.0343 (13)	−0.0048 (10)	−0.0016 (10)	0.0051 (10)
C3	0.0321 (13)	0.0313 (13)	0.0359 (13)	0.0059 (10)	0.0073 (10)	0.0000 (10)
C4	0.0166 (10)	0.0317 (12)	0.0213 (11)	−0.0010 (9)	0.0029 (8)	0.0025 (9)
C5	0.0269 (11)	0.0318 (12)	0.0291 (12)	−0.0049 (10)	0.0025 (9)	−0.0009 (10)
C6	0.0263 (11)	0.0376 (13)	0.0215 (11)	0.0024 (10)	0.0053 (9)	0.0026 (9)
N2	0.0212 (9)	0.0194 (9)	0.0155 (9)	−0.0006 (7)	0.0024 (7)	0.0016 (7)
C7	0.0250 (11)	0.0193 (10)	0.0223 (11)	0.0033 (8)	0.0058 (8)	0.0025 (8)
C8	0.0389 (13)	0.0276 (12)	0.0252 (12)	0.0062 (10)	0.0127 (10)	0.0012 (9)
C9	0.0229 (11)	0.0302 (12)	0.0362 (13)	0.0018 (9)	0.0047 (9)	0.0045 (10)
C10	0.0210 (10)	0.0280 (11)	0.0184 (10)	0.0003 (9)	−0.0011 (8)	0.0025 (8)
C11	0.0237 (11)	0.0291 (12)	0.0336 (13)	−0.0043 (9)	−0.0004 (9)	−0.0029 (10)
C12	0.0239 (11)	0.0284 (12)	0.0359 (13)	0.0029 (9)	0.0072 (9)	0.0058 (10)
S1	0.0346 (3)	0.0204 (3)	0.0242 (3)	−0.0009 (2)	0.0028 (2)	−0.0015 (2)
S2	0.0162 (3)	0.0206 (3)	0.0155 (3)	−0.00044 (19)	0.00114 (18)	0.00144 (18)
O1	0.0258 (8)	0.0300 (8)	0.0200 (7)	−0.0005 (6)	0.0060 (6)	−0.0045 (6)
O2	0.0346 (8)	0.0219 (8)	0.0177 (7)	−0.0020 (6)	0.0007 (6)	0.0030 (6)
O3	0.0166 (7)	0.0340 (9)	0.0374 (9)	−0.0010 (6)	−0.0015 (6)	0.0017 (7)

Geometric parameters (Å, º)

N1—C4	1.504 (3)	N2—H2N	0.853 (10)
N1—C1	1.507 (3)	N2—H2M	0.846 (10)
N1—H1N	0.853 (10)	C7—C8	1.522 (3)
N1—H1M	0.844 (10)	C7—C9	1.523 (3)
C1—C2	1.511 (3)	C7—H7	1
C1—C3	1.517 (3)	C8—H8A	0.98
C1—H1	1	C8—H8B	0.98
C2—H2A	0.98	C8—H8C	0.98
C2—H2B	0.98	C9—H9A	0.98
C2—H2C	0.98	C9—H9B	0.98

C3—H3A	0.98	C9—H9C	0.98
C3—H3B	0.98	C10—C12	1.516 (3)
C3—H3C	0.98	C10—C11	1.518 (3)
C4—C6	1.516 (3)	C10—H10	1
C4—C5	1.517 (3)	C11—H11A	0.98
C4—H4	1	C11—H11B	0.98
C5—H5A	0.98	C11—H11C	0.98
C5—H5B	0.98	C12—H12A	0.98
C5—H5C	0.98	C12—H12B	0.98
C6—H6A	0.98	C12—H12C	0.98
C6—H6B	0.98	S1—S2	1.9898 (7)
C6—H6C	0.98	S2—O3	1.4713 (15)
N2—C7	1.504 (3)	S2—O1	1.4743 (15)
N2—C10	1.505 (3)	S2—O2	1.4756 (15)

C4—N1—C1	118.03 (16)	C7—N2—H2M	108.0 (17)
C4—N1—H1N	107.0 (16)	C10—N2—H2M	108.3 (16)
C1—N1—H1N	107.6 (16)	H2N—N2—H2M	110 (2)
C4—N1—H1M	107.2 (17)	N2—C7—C8	110.31 (17)
C1—N1—H1M	108.4 (17)	N2—C7—C9	106.84 (17)
H1N—N1—H1M	108 (2)	C8—C7—C9	112.29 (18)
N1—C1—C2	107.78 (17)	N2—C7—H7	109.1
N1—C1—C3	111.30 (18)	C8—C7—H7	109.1
C2—C1—C3	112.37 (19)	C9—C7—H7	109.1
N1—C1—H1	108.4	C7—C8—H8A	109.5
C2—C1—H1	108.4	C7—C8—H8B	109.5
C3—C1—H1	108.4	H8A—C8—H8B	109.5
C1—C2—H2A	109.5	C7—C8—H8C	109.5
C1—C2—H2B	109.5	H8A—C8—H8C	109.5
H2A—C2—H2B	109.5	H8B—C8—H8C	109.5
C1—C2—H2C	109.5	C7—C9—H9A	109.5
H2A—C2—H2C	109.5	C7—C9—H9B	109.5
H2B—C2—H2C	109.5	H9A—C9—H9B	109.5
C1—C3—H3A	109.5	C7—C9—H9C	109.5
C1—C3—H3B	109.5	H9A—C9—H9C	109.5
H3A—C3—H3B	109.5	H9B—C9—H9C	109.5
C1—C3—H3C	109.5	N2—C10—C12	107.13 (17)
H3A—C3—H3C	109.5	N2—C10—C11	111.26 (17)
H3B—C3—H3C	109.5	C12—C10—C11	112.68 (18)
N1—C4—C6	110.87 (17)	N2—C10—H10	108.6
N1—C4—C5	107.58 (17)	C12—C10—H10	108.6
C6—C4—C5	112.12 (19)	C11—C10—H10	108.6
N1—C4—H4	108.7	C10—C11—H11A	109.5
C6—C4—H4	108.7	C10—C11—H11B	109.5
C5—C4—H4	108.7	H11A—C11—H11B	109.5
C4—C5—H5A	109.5	C10—C11—H11C	109.5
C4—C5—H5B	109.5	H11A—C11—H11C	109.5
H5A—C5—H5B	109.5	H11B—C11—H11C	109.5
C4—C5—H5C	109.5	C10—C12—H12A	109.5

H5A—C5—H5C	109.5	C10—C12—H12B	109.5
H5B—C5—H5C	109.5	H12A—C12—H12B	109.5
C4—C6—H6A	109.5	C10—C12—H12C	109.5
C4—C6—H6B	109.5	H12A—C12—H12C	109.5
H6A—C6—H6B	109.5	H12B—C12—H12C	109.5
C4—C6—H6C	109.5	O3—S2—O1	109.16 (9)
H6A—C6—H6C	109.5	O3—S2—O2	110.01 (9)
H6B—C6—H6C	109.5	O1—S2—O2	109.50 (9)
C7—N2—C10	118.09 (16)	O3—S2—S1	110.50 (7)
C7—N2—H2N	107.6 (16)	O1—S2—S1	109.77 (7)
C10—N2—H2N	104.7 (16)	O2—S2—S1	107.87 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*M*···O1^{i}	0.84 (1)	1.95 (1)	2.764 (2)	161 (2)
N1—H1*N*···O3	0.85 (1)	1.94 (1)	2.774 (2)	165 (2)
N2—H2*N*···O2	0.85 (1)	1.88 (1)	2.737 (2)	178 (2)
N2—H2*M*···S1^{ii}	0.85 (1)	2.55 (1)	3.3688 (17)	164 (2)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+3/2, y-1/2, -z+1/2$.

(II) Bis(*tert*-butylammonium) thiosulfate

Crystal data

$2C_4H_{12}N^+\cdot S_2O_3^{2-}$
$M_r = 260.41$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 11.7834$ (4) Å
$b = 12.3519$ (6) Å
$c = 19.9312$ (8) Å
$\beta = 97.017$ (4)°
$V = 2879.2$ (2) Å^3
$Z = 8$

$F(000) = 1136$
$D_x = 1.202$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6114 reflections
$\theta = 2.1–28.8°$
$\mu = 0.36$ mm^{-1}
$T = 120$ K
Prism, colourless
0.54 × 0.12 × 0.03 mm

Data collection

Oxford Diffraction Xcalibur (Sapphire2, large Be window) diffractometer
Graphite monochromator
Detector resolution: 8.1883 pixels mm^{-1}
ω scans
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010), based on expressions derived by Clark & Reid (1995)]

$T_{min} = 0.834$, $T_{max} = 0.986$
10821 measured reflections
5063 independent reflections
3704 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 25°$, $\theta_{min} = 2.4°$
$h = -13 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$

$S = 0.96$
5063 reflections
331 parameters
12 restraints

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.60140 (14)	0.26074 (14)	0.31094 (8)	0.0174 (4)
C1	0.58808 (15)	0.22664 (16)	0.38228 (9)	0.0192 (4)
C2	0.53094 (17)	0.32054 (17)	0.41466 (9)	0.0274 (5)
H2A	0.5772	0.3861	0.4125	0.033*
H2B	0.5242	0.3032	0.462	0.033*
H2C	0.4546	0.3327	0.3903	0.033*
C3	0.51377 (16)	0.12543 (17)	0.37739 (10)	0.0242 (5)
H3A	0.4385	0.1425	0.3532	0.029*
H3B	0.5048	0.0997	0.423	0.029*
H3C	0.5502	0.0689	0.3529	0.029*
C4	0.70735 (16)	0.20306 (18)	0.41860 (9)	0.0280 (5)
H4A	0.7416	0.143	0.396	0.034*
H4B	0.7016	0.1834	0.4657	0.034*
H4C	0.7553	0.2677	0.4174	0.034*
H1M	0.6384 (15)	0.2156 (14)	0.2900 (9)	0.028 (6)*
H1N	0.5361 (10)	0.2658 (17)	0.2875 (8)	0.028 (6)*
H1O	0.6340 (15)	0.3214 (10)	0.3088 (9)	0.021 (6)*
N2	0.40549 (14)	0.52191 (14)	0.19686 (8)	0.0180 (4)
C5	0.42213 (16)	0.54972 (17)	0.12514 (9)	0.0218 (4)
C6	0.49084 (19)	0.45693 (19)	0.09964 (10)	0.0327 (5)
H6A	0.5638	0.4499	0.1287	0.039*
H6B	0.5053	0.4719	0.0532	0.039*
H6C	0.4475	0.3894	0.1007	0.039*
C7	0.48764 (17)	0.65643 (18)	0.12711 (11)	0.0325 (5)
H7A	0.4433	0.713	0.1466	0.039*
H7B	0.5001	0.677	0.0811	0.039*
H7C	0.5616	0.6479	0.1549	0.039*
C8	0.30479 (17)	0.5606 (2)	0.08455 (10)	0.0329 (5)
H8A	0.261	0.494	0.0889	0.039*
H8B	0.3135	0.5728	0.0369	0.039*
H8C	0.2642	0.6219	0.1018	0.039*
H2M	0.3764 (15)	0.4580 (10)	0.1990 (9)	0.020 (5)*
H2N	0.3618 (15)	0.5653 (14)	0.2144 (9)	0.032 (6)*

H2O	0.4698 (11)	0.5195 (18)	0.2216 (9)	0.033 (6)*
N3	0.62268 (14)	0.77725 (15)	0.32429 (8)	0.0171 (4)
C9	0.65158 (15)	0.75167 (15)	0.39848 (8)	0.0170 (4)
C10	0.59792 (17)	0.64271 (16)	0.41156 (9)	0.0248 (5)
H10A	0.5148	0.6473	0.4002	0.03*
H10B	0.6162	0.6236	0.4594	0.03*
H10C	0.6283	0.5871	0.3835	0.03*
C11	0.60398 (16)	0.84248 (16)	0.43859 (9)	0.0228 (4)
H11A	0.6415	0.9108	0.4295	0.027*
H11B	0.6183	0.826	0.487	0.027*
H11C	0.5215	0.849	0.4251	0.027*
C12	0.78131 (15)	0.74653 (17)	0.41278 (9)	0.0249 (5)
H12A	0.8098	0.6876	0.3865	0.03*
H12B	0.8036	0.7333	0.4611	0.03*
H12C	0.814	0.8153	0.4	0.03*
H3M	0.6522 (15)	0.7323 (13)	0.2991 (8)	0.022 (6)*
H3N	0.6554 (15)	0.8364 (11)	0.3162 (9)	0.025 (6)*
H3O	0.5505 (8)	0.7800 (17)	0.3116 (9)	0.021 (5)*
N4	0.37223 (14)	0.00434 (15)	0.17111 (8)	0.0177 (4)
C13	0.34307 (15)	0.03858 (16)	0.09815 (9)	0.0186 (4)
C14	0.40860 (17)	0.14174 (17)	0.08805 (10)	0.0274 (5)
H14A	0.3857	0.1982	0.1182	0.033*
H14B	0.3917	0.1657	0.041	0.033*
H14C	0.4908	0.1281	0.0984	0.033*
C15	0.37825 (17)	−0.05355 (17)	0.05410 (9)	0.0253 (5)
H15A	0.4601	−0.0681	0.0654	0.03*
H15B	0.3627	−0.033	0.0064	0.03*
H15C	0.3346	−0.1188	0.0622	0.03*
C16	0.21438 (16)	0.05722 (18)	0.08617 (10)	0.0281 (5)
H16A	0.1746	−0.009	0.0971	0.034*
H16B	0.1919	0.0762	0.0387	0.034*
H16C	0.1938	0.1165	0.1151	0.034*
H4M	0.3407 (14)	−0.0555 (10)	0.1801 (9)	0.016 (5)*
H4N	0.3513 (17)	0.0494 (14)	0.1991 (8)	0.029 (6)*
H4O	0.4438 (9)	−0.0048 (17)	0.1819 (9)	0.023 (6)*
S1	0.15473 (4)	0.34224 (4)	0.18497 (2)	0.02517 (14)
S2	0.26742 (4)	0.27043 (4)	0.25350 (2)	0.01713 (12)
O1	0.24868 (11)	0.30692 (11)	0.32133 (6)	0.0238 (3)
O2	0.25535 (10)	0.15144 (11)	0.24898 (6)	0.0220 (3)
O3	0.38325 (10)	0.30081 (11)	0.23862 (6)	0.0230 (3)
S3	0.84944 (4)	0.43865 (5)	0.32669 (2)	0.02598 (14)
S4	0.74355 (4)	0.51268 (4)	0.25539 (2)	0.01690 (12)
O4	0.75859 (11)	0.63157 (11)	0.25980 (6)	0.0233 (3)
O5	0.62567 (10)	0.48561 (11)	0.26739 (6)	0.0221 (3)
O6	0.76708 (11)	0.47533 (11)	0.18864 (6)	0.0234 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0177 (9)	0.0115 (10)	0.0241 (9)	−0.0021 (8)	0.0066 (7)	−0.0006 (7)

C1	0.0198 (9)	0.0184 (11)	0.0204 (9)	0.0002 (9)	0.0059 (8)	0.0014 (8)
C2	0.0336 (11)	0.0226 (12)	0.0276 (10)	0.0010 (10)	0.0100 (9)	−0.0027 (9)
C3	0.0250 (10)	0.0184 (12)	0.0307 (11)	0.0009 (9)	0.0088 (8)	0.0054 (9)
C4	0.0237 (10)	0.0328 (13)	0.0276 (10)	0.0002 (10)	0.0035 (8)	0.0018 (10)
N2	0.0176 (9)	0.0130 (10)	0.0241 (9)	0.0002 (8)	0.0053 (7)	0.0021 (7)
C5	0.0225 (10)	0.0211 (12)	0.0228 (10)	0.0043 (9)	0.0071 (8)	0.0075 (8)
C6	0.0417 (13)	0.0314 (14)	0.0264 (11)	0.0111 (11)	0.0104 (10)	0.0012 (10)
C7	0.0284 (11)	0.0276 (14)	0.0435 (12)	0.0045 (10)	0.0124 (10)	0.0161 (11)
C8	0.0291 (11)	0.0425 (15)	0.0271 (11)	0.0059 (11)	0.0039 (9)	0.0069 (10)
N3	0.0170 (9)	0.0151 (10)	0.0199 (8)	−0.0002 (8)	0.0050 (7)	0.0005 (7)
C9	0.0206 (10)	0.0143 (10)	0.0166 (9)	−0.0019 (8)	0.0043 (7)	0.0016 (8)
C10	0.0309 (11)	0.0184 (11)	0.0263 (10)	−0.0040 (10)	0.0082 (9)	0.0026 (9)
C11	0.0250 (10)	0.0226 (12)	0.0208 (9)	0.0020 (9)	0.0029 (8)	−0.0040 (9)
C12	0.0209 (10)	0.0254 (12)	0.0281 (10)	0.0010 (9)	0.0017 (8)	0.0051 (9)
N4	0.0181 (9)	0.0143 (10)	0.0214 (9)	−0.0014 (8)	0.0054 (7)	−0.0004 (8)
C13	0.0207 (10)	0.0168 (11)	0.0182 (9)	−0.0019 (8)	0.0018 (8)	0.0006 (8)
C14	0.0343 (11)	0.0199 (12)	0.0283 (10)	−0.0062 (10)	0.0054 (9)	0.0038 (9)
C15	0.0312 (11)	0.0235 (12)	0.0216 (10)	−0.0004 (10)	0.0045 (8)	−0.0045 (9)
C16	0.0222 (10)	0.0287 (13)	0.0324 (11)	0.0011 (10)	−0.0003 (9)	0.0010 (10)
S1	0.0197 (3)	0.0255 (3)	0.0294 (3)	0.0007 (2)	−0.0005 (2)	0.0031 (2)
S2	0.0171 (2)	0.0118 (3)	0.0233 (2)	−0.0001 (2)	0.00557 (18)	−0.0007 (2)
O1	0.0295 (7)	0.0174 (8)	0.0248 (7)	0.0037 (6)	0.0043 (6)	−0.0018 (6)
O2	0.0247 (7)	0.0129 (7)	0.0305 (7)	−0.0013 (6)	0.0116 (6)	−0.0013 (6)
O3	0.0154 (6)	0.0207 (8)	0.0331 (7)	−0.0023 (6)	0.0045 (6)	0.0044 (6)
S3	0.0197 (3)	0.0273 (3)	0.0304 (3)	0.0002 (2)	0.0008 (2)	0.0058 (2)
S4	0.0186 (2)	0.0107 (3)	0.0225 (2)	−0.0007 (2)	0.00668 (18)	0.00005 (19)
O4	0.0297 (7)	0.0120 (7)	0.0309 (7)	−0.0005 (6)	0.0147 (6)	−0.0026 (6)
O5	0.0174 (7)	0.0196 (8)	0.0298 (7)	−0.0007 (6)	0.0050 (6)	0.0046 (6)
O6	0.0297 (7)	0.0177 (8)	0.0241 (7)	0.0014 (6)	0.0080 (6)	−0.0008 (6)

Geometric parameters (Å, º)

N1—C1	1.509 (2)	C9—C12	1.522 (2)
N1—H1M	0.848 (9)	C9—C10	1.523 (3)
N1—H1N	0.853 (9)	C9—C11	1.524 (2)
N1—H1O	0.845 (9)	C10—H10A	0.98
C1—C3	1.523 (3)	C10—H10B	0.98
C1—C2	1.524 (3)	C10—H10C	0.98
C1—C4	1.528 (2)	C11—H11A	0.98
C2—H2A	0.98	C11—H11B	0.98
C2—H2B	0.98	C11—H11C	0.98
C2—H2C	0.98	C12—H12A	0.98
C3—H3A	0.98	C12—H12B	0.98
C3—H3B	0.98	C12—H12C	0.98
C3—H3C	0.98	N4—C13	1.513 (2)
C4—H4A	0.98	N4—H4M	0.856 (9)
C4—H4B	0.98	N4—H4N	0.845 (9)
C4—H4C	0.98	N4—H4O	0.852 (9)
N2—C5	1.506 (2)	C13—C14	1.516 (3)
N2—H2M	0.864 (9)	C13—C16	1.524 (2)

N2—H2N	0.848 (9)	C13—C15	1.525 (3)
N2—H2O	0.853 (9)	C14—H14A	0.98
C5—C8	1.520 (3)	C14—H14B	0.98
C5—C7	1.526 (3)	C14—H14C	0.98
C5—C6	1.526 (3)	C15—H15A	0.98
C6—H6A	0.98	C15—H15B	0.98
C6—H6B	0.98	C15—H15C	0.98
C6—H6C	0.98	C16—H16A	0.98
C7—H7A	0.98	C16—H16B	0.98
C7—H7B	0.98	C16—H16C	0.98
C7—H7C	0.98	S1—S2	1.9932 (7)
C8—H8A	0.98	S2—O1	1.4671 (13)
C8—H8B	0.98	S2—O2	1.4784 (14)
C8—H8C	0.98	S2—O3	1.4800 (12)
N3—C9	1.510 (2)	S3—S4	1.9949 (7)
N3—H3M	0.852 (9)	S4—O6	1.4662 (13)
N3—H3N	0.850 (9)	S4—O5	1.4763 (13)
N3—H3O	0.857 (9)	S4—O4	1.4805 (14)

C1—N1—H1M	113.5 (14)	N3—C9—C12	107.06 (14)
C1—N1—H1N	110.2 (13)	N3—C9—C10	107.70 (15)
H1M—N1—H1N	105.2 (19)	C12—C9—C10	111.08 (16)
C1—N1—H1O	113.2 (13)	N3—C9—C11	107.84 (15)
H1M—N1—H1O	107.1 (18)	C12—C9—C11	110.99 (16)
H1N—N1—H1O	107.1 (19)	C10—C9—C11	111.93 (15)
N1—C1—C3	107.10 (15)	C9—C10—H10A	109.5
N1—C1—C2	106.79 (16)	C9—C10—H10B	109.5
C3—C1—C2	111.82 (15)	H10A—C10—H10B	109.5
N1—C1—C4	107.70 (15)	C9—C10—H10C	109.5
C3—C1—C4	111.23 (16)	H10A—C10—H10C	109.5
C2—C1—C4	111.89 (16)	H10B—C10—H10C	109.5
C1—C2—H2A	109.5	C9—C11—H11A	109.5
C1—C2—H2B	109.5	C9—C11—H11B	109.5
H2A—C2—H2B	109.5	H11A—C11—H11B	109.5
C1—C2—H2C	109.5	C9—C11—H11C	109.5
H2A—C2—H2C	109.5	H11A—C11—H11C	109.5
H2B—C2—H2C	109.5	H11B—C11—H11C	109.5
C1—C3—H3A	109.5	C9—C12—H12A	109.5
C1—C3—H3B	109.5	C9—C12—H12B	109.5
H3A—C3—H3B	109.5	H12A—C12—H12B	109.5
C1—C3—H3C	109.5	C9—C12—H12C	109.5
H3A—C3—H3C	109.5	H12A—C12—H12C	109.5
H3B—C3—H3C	109.5	H12B—C12—H12C	109.5
C1—C4—H4A	109.5	C13—N4—H4M	112.9 (12)
C1—C4—H4B	109.5	C13—N4—H4N	113.5 (14)
H4A—C4—H4B	109.5	H4M—N4—H4N	105.2 (18)
C1—C4—H4C	109.5	C13—N4—H4O	112.4 (13)
H4A—C4—H4C	109.5	H4M—N4—H4O	105.9 (19)
H4B—C4—H4C	109.5	H4N—N4—H4O	106.3 (19)

C5—N2—H2M	110.7 (12)	N4—C13—C14	107.64 (15)
C5—N2—H2N	113.8 (14)	N4—C13—C16	107.31 (14)
H2M—N2—H2N	107.0 (19)	C14—C13—C16	111.44 (17)
C5—N2—H2O	110.4 (14)	N4—C13—C15	107.39 (16)
H2M—N2—H2O	106 (2)	C14—C13—C15	111.84 (15)
H2N—N2—H2O	109 (2)	C16—C13—C15	110.96 (16)
N2—C5—C8	108.05 (15)	C13—C14—H14A	109.5
N2—C5—C7	107.26 (16)	C13—C14—H14B	109.5
C8—C5—C7	111.22 (17)	H14A—C14—H14B	109.5
N2—C5—C6	106.30 (16)	C13—C14—H14C	109.5
C8—C5—C6	111.98 (18)	H14A—C14—H14C	109.5
C7—C5—C6	111.73 (17)	H14B—C14—H14C	109.5
C5—C6—H6A	109.5	C13—C15—H15A	109.5
C5—C6—H6B	109.5	C13—C15—H15B	109.5
H6A—C6—H6B	109.5	H15A—C15—H15B	109.5
C5—C6—H6C	109.5	C13—C15—H15C	109.5
H6A—C6—H6C	109.5	H15A—C15—H15C	109.5
H6B—C6—H6C	109.5	H15B—C15—H15C	109.5
C5—C7—H7A	109.5	C13—C16—H16A	109.5
C5—C7—H7B	109.5	C13—C16—H16B	109.5
H7A—C7—H7B	109.5	H16A—C16—H16B	109.5
C5—C7—H7C	109.5	C13—C16—H16C	109.5
H7A—C7—H7C	109.5	H16A—C16—H16C	109.5
H7B—C7—H7C	109.5	H16B—C16—H16C	109.5
C5—C8—H8A	109.5	O1—S2—O2	109.72 (7)
C5—C8—H8B	109.5	O1—S2—O3	110.68 (8)
H8A—C8—H8B	109.5	O2—S2—O3	108.91 (8)
C5—C8—H8C	109.5	O1—S2—S1	109.40 (6)
H8A—C8—H8C	109.5	O2—S2—S1	110.46 (6)
H8B—C8—H8C	109.5	O3—S2—S1	107.66 (6)
C9—N3—H3M	112.4 (13)	O6—S4—O5	111.21 (8)
C9—N3—H3N	108.2 (13)	O6—S4—O4	109.37 (7)
H3M—N3—H3N	102.8 (18)	O5—S4—O4	108.85 (8)
C9—N3—H3O	113.2 (12)	O6—S4—S3	109.33 (6)
H3M—N3—H3O	108.4 (18)	O5—S4—S3	107.44 (6)
H3N—N3—H3O	111.5 (19)	O4—S4—S3	110.64 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*M*···O4^{i}	0.85 (1)	1.96 (1)	2.797 (2)	170 (2)
N1—H1*N*···O3	0.85 (1)	1.99 (1)	2.833 (2)	171 (2)
N1—H1*O*···O5	0.85 (1)	2.19 (1)	2.934 (2)	147 (2)
N2—H2*M*···O3	0.86 (1)	2.09 (1)	2.876 (2)	150 (2)
N2—H2*N*···O2^{ii}	0.85 (1)	1.95 (1)	2.796 (2)	172 (2)
N2—H2*O*···O5	0.85 (1)	1.99 (1)	2.832 (2)	168 (2)
N3—H3*M*···O4	0.85 (1)	1.99 (1)	2.821 (2)	164 (2)
N3—H3*N*···O6^{iii}	0.85 (1)	1.95 (1)	2.797 (2)	172 (2)
N3—H3*O*···S1^{ii}	0.86 (1)	2.55 (1)	3.3491 (17)	156 (2)

N4—H4*M*···O1^{iv}	0.86 (1)	2.00 (1)	2.837 (2)	167 (2)
N4—H4*N*···O2	0.85 (1)	2.03 (1)	2.851 (2)	163 (2)
N4—H4*O*···S3^{i}	0.85 (1)	2.56 (1)	3.3737 (17)	160 (2)

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