Phase transition and structures of the twinned low-temperature phases of $(Et_4N)[ReS_4]$

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The title compound, tetraethylammonium tetrathiorhenate, $[(C_2H_5)_4N][ReS_4]$, has, at room temperature, a disordered structure in the space group $P6_3mc$ ($Z = 2$, α-phase). A phase transition to the monoclinic space group $P2_1$ ($Z = 2$, γ-phase) at 285 K leads to a pseudo-merohedral twin. The high deviation from the hexagonal metric causes split reflections. However, the different orientations could not be separated, but were integrated using a large integration box. Rapid cooling to 110–170 K produces a metastable β-phase ($P6_3$, $Z = 18$) in addition to the γ-phase. All crystals of the β-phase are contaminated with the γ-phase. Additionally, the crystals of the β-phase are merohedrally twinned. In contrast to the α-phase, the β- and γ-phases do not show disorder.

1. Introduction

Salts with the ReS_4^- anion were synthesized for the first time in 1970 (Müller *et al.*, 1970). So far, some syntheses of ReS_4^- salts with different cations, such as Me_4N^+ (Müller *et al.*, 1970), Ph_4P^+ (Müller *et al.*, 1970), Ph_4As^+ (Müller *et al.*, 1970; Halbert *et al.*, 1990; Wei *et al.*, 1991), Bu_4N^+ (Do *et al.*, 1985), Et_4N^+ (Müller *et al.*, 1986, 1987; Halbert *et al.*, 1990; Wei *et al.*, 1991; Goodman & Rauchfuss, 2002), Pr_4N^+ (Scattergood *et al.*, 1987) and $(PhCH_2)Et_3N^+$ (Halbert *et al.*, 1990; Wei *et al.*, 1991), have been reported. There is a lack of reliable methods to prepare salts of the ReS_4^- anion with Na^+, K^+, Rb^+ and Cs^+ cations. The ReS_4^- anion is used in several organic chemistry reactions, such as addition reactions to carbon–carbon multiple bonds (Goodman *et al.*, 1996; Goodman & Rauchfuss, 1998, 1999; Dopke *et al.*, 2000) and the carbon–nitrogen triple bond of some nitriles (Goodman & Rauchfuss, 1997). Moreover, the reaction of the ReS_4^- anion with isonitriles has been described (Schwarz & Rauchfuss, 2000).
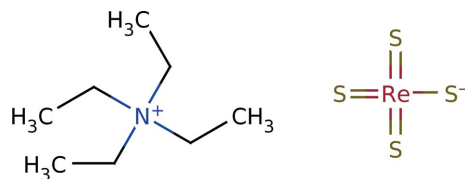
Phases **Ia/Ib/Ic**

X-ray diffraction studies were published for Ph_4PReS_4 (Müller *et al.*, 1970; Diemann & Müller, 1976), Ph_4AsReS_4 (Müller *et al.*, 1970), Bu_4NReS_4 (Do *et al.*, 1985) and Et_4NReS_4 (Müller *et al.*, 1986, 1987). While the structures of Ph_4PReS_4, Ph_4AsReS_4 and Bu_4NReS_4 are ordered, the structure of Et_4NReS_4 [$P6mm$, $a = 8.149$ (2), $c = 6.538$ (1) Å, $Z = 1$, room temperature] is disordered. Superstructural reflections were observed, suggesting a larger unit cell. The aim of this work
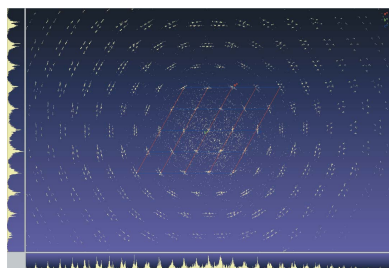
Table 1
Experimental details.

For all phases: $(C_8H_{20}N)[ReS_4]$, $M_r = 444.69$. Experiments were carried out with Mo $K\alpha$ radiation using an Oxford Diffraction Gemini E Ultra diffractometer with an EOS CCD camera. The absorption correction was analytical [*CrysAlis PRO* (Agilent, 2013), based on expressions derived by Clark & Reid (1995)]. H-atom parameters were constrained.

	Ia	Ib	Ic
Crystal data			
Crystal system, space group	Hexagonal, $P6_3mc$	Hexagonal, $P6_3$	Monoclinic, $P2_1$
Temperature (K)	297	110	150
a, b, c (Å)	8.150 (2), 8.150 (3), 13.092 (3)	24.170 (3), 24.170 (3), 12.916 (2)	7.900 (2), 12.842 (3), 8.118 (2)
α, β, γ (°)	90, 90, 120	90, 90, 120	90, 119.04 (2), 90
V (Å³)	753.1 (4)	6534.5 (19)	720.0 (3)
Z	2	18	2
μ (mm⁻¹)	8.59	8.91	8.99
Crystal size (mm)	$0.32 \times 0.03 \times 0.03$	$0.24 \times 0.21 \times 0.16$	$0.24 \times 0.20 \times 0.17$
Data collection			
T_{min}, T_{max}	0.599, 0.829	0.253, 0.351	0.241, 0.336
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1804, 513, 392	44958, 9707, 8807	4476, 2814, 2808
R_{int}	0.029	0.036	0.053
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.632	0.696	0.688
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.048, 1.08	0.028, 0.048, 1.05	0.052, 0.138, 1.09
No. of reflections	513	9707	2814
No. of parameters	44	380	87
No. of restraints	34	1	89
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.26, −0.42	0.87, −1.09	2.01, −4.80
Absolute structure	Refined as an inversion twin	Twinning involves mirror, so Flack parameter cannot be determined	Twinning involves mirror, so Flack parameter cannot be determined
Absolute structure parameter	0.14 (4) (Parsons *et al.*, 2013)	–	–

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2001).

was to verify that the unit cell of Et_4NReS_4 would be larger at room temperature. Another goal of this work was to investigate whether a phase transition to an ordered structure could be observed at lower temperatures.

2. Experimental

2.1. Synthesis and crystallization

Et_4NReS_4 was synthesized according to the literature method of Goodman & Rauchfuss (2002). Slow evaporation of an acetonitrile solution of Et_4NReS_4 in air afforded crystals suitable for X-ray diffraction analysis.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The phase designations **Ia**–**Ic** are analogous to that used for Et_4NFeCl_4 (Lutz *et al.*, 2014).

2.2.1. α-phase. The crystal structure of the α-phase (denoted **Ia**) at 297 K was refined in the space group $P6_3mc$ (Table 1) starting from the structure of Et_4NFeCl_4 at 290 K (Lutz *et al.*, 2014). The ReS_4^- anion is completely ordered. The whole tetraethylammonium cation is disordered about special position b with $3m$ symmetry. A whole cation with an occupancy of 1/6 was modelled. Similarity distance restraints were applied for the ethyl groups. All the atoms of the cation were refined isotropically because of this severe disorder, whereas the atoms of the ordered anion were refined anisotropically (Fig. 1a). H atoms were attached to geometrically

optimized positions and refined with the riding model. Twinning by inversion was considered. The fractional contribution of the minor domain refined to 0.14 (4). The C—H distances were fixed at 0.96 (CH_3) or 0.97 Å (CH_2). The U_{iso}(H) values were constrained to $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) otherwise.

2.2.2. γ-phase. Upon slow cooling (*ca* 5 K min⁻¹) to 285 K, crystals of the α-phase (*i.e.* **Ia**) undergo a reversible phase transition to the γ-phase (denoted **Ic**). No further phase transitions could be observed between 110 and 300 K. The γ-phase crystallizes in the space group $P2_1$ as a pseudomerohedral twin (Table 1). Attempts to grow crystals at 273 and 253 K also led to the formation of twins. Data for the γ-phase were collected at 150 K. The high deviation from the hexagonal metric leads to split reflections and reflections of different domains close to each other (see Fig. S1 of the supporting information). However, the different orientations could not be separated. To take the twinning into account, an *HKLF5* file (Sevvana *et al.*, 2019) was produced (*SHELXL-2018*; Sheldrick, 2015) according to the transition from $P6_3mc$ to $P2_1$ (Table 2). The normal procedure using the TWIN command was not possible, because in *SHELXL*, only one TWIN command is allowed, but here two twin operations, a threefold and a mirror, are needed. We checked for additional twinning by inversion using now twelve components, but the fractional contributions of the additional six components refined to values close to zero (for details, see the supporting information). Both the tetrathioperrhenate anion (ReS_4^-) and

Table 2
Twin components in **Ic**.

Twin components	Appropriate symmetry operations in $P6_3mc$	$h,k,l;i$ $[i = -h-l]^*$	Fractional contribution k_i
1	[1] 1	$h,k,l;i$	0.178 (7)
2	[2] 3^+ (0,0,z)	$l,k,i;h$	0.213 (7)
3	[3] 3^- (0,0,z)	$i,k,h;l$	0.080 (7)
4	[7] m (x,−x,z)	$-l,k,-h;i$	0.084 (7)
5	[8] m (x,2x,z)	$-h,k,-i;l$	0.233 (7)
6	[9] m (2x,x,z)	$-i,k,-l;h$	0.212 (7)

Note: (*) the fourth Miller index is the sum of $-h$ and $-l$, because the transformation from $P6_3mc$ to $P2_1$ causes the 6_3-axis along the y axis.

the tetraethylammonium cation are completely ordered (Fig. 1b). However, to stabilize the refinement, distance restraints were used and the cation was only isotropically refined. H atoms were attached to geometrical optimized positions and refined with the riding model. The C—H distances were fixed at 0.98 (CH$_3$) or 0.99 Å (CH$_2$). The U_{iso}(H) values were constrained to 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) otherwise.

2.2.3. β-phase. Rapid cooling (>100 K s^{-1}) of the α-phase (*i.e.* **Ia**) to 110–170 K leads to a mixture of the γ-phase (*i.e.* **Ic**) and the β-phase (denoted **Ib**) through a phase transition forming an allotwin. A reciprocal space plot (see Fig. S2 in the supporting information) shows satellites for the reflections with $h = 3n$ and $k = 3m$. With slow heating (*ca* 5 K min^{-1}) to 200 K, the β-phase irreversibly changes to the γ-phase. We were not able to obtain crystals of the β-phase free from the γ-phase. Such a superposition of reflections of two phases was also found, for example, in Kautny *et al.* (2017). The a and b axes of the β-phase are enlarged by a factor of three compared to the γ-phase. Therefore, all *hkl* reflections with $h = 3n$ and $k = 3m$ of the β-phase are contaminated with reflections of the γ-phase. The data collection software (*CrysAlis PRO*; Oxford Diffraction, 2016) could not split the summed intensity into its two components. Therefore, the *hkl* reflections with $h = 3n$ and $k = 3m$ had to be removed from the data set. This lowers the completeness to only 88.8%. Including the contaminated reflections raises the *R*1 value from 0.0354 to 0.0548 and shows F_{obs}^2 values for *hkl* reflections with $h = 3n$ and $k = 3m$ much bigger than the F_{calc}^2 values (see Table S1 in the supporting information). Even with the ISOR restraint, where atoms are restrained with effective standard deviations so that their U^{ij} components approximate to isotropic behaviour, the aniso-tropic displacement parameters refine to nonpositive definite values and the residual density increases to 3.45/−3.41 e Å^{-3}. The C—H distances were fixed at 0.98 (CH$_3$) or 0.99 Å (CH$_2$). The U_{iso}(H) values were constrained to 1.5U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) otherwise.

The β-phase of Et$_4$NReS$_4$ is isostructural with Et$_4$NFeCl$_4$ at 230 K (Lutz *et al.*, 2014). It crystallizes as a merohedral twin with the twin law 010 100 001 and a fractional contribution of 0.5005 (15). This twin law describes a mirror plane perpendicular to the face diagonal. To check for additional twinning by inversion, a refinement with 'TWIN 0 1 0 1 0 0 0 0 1 −4' was applied. The additional fractional contributions refined to

(a)

(b)

(c)
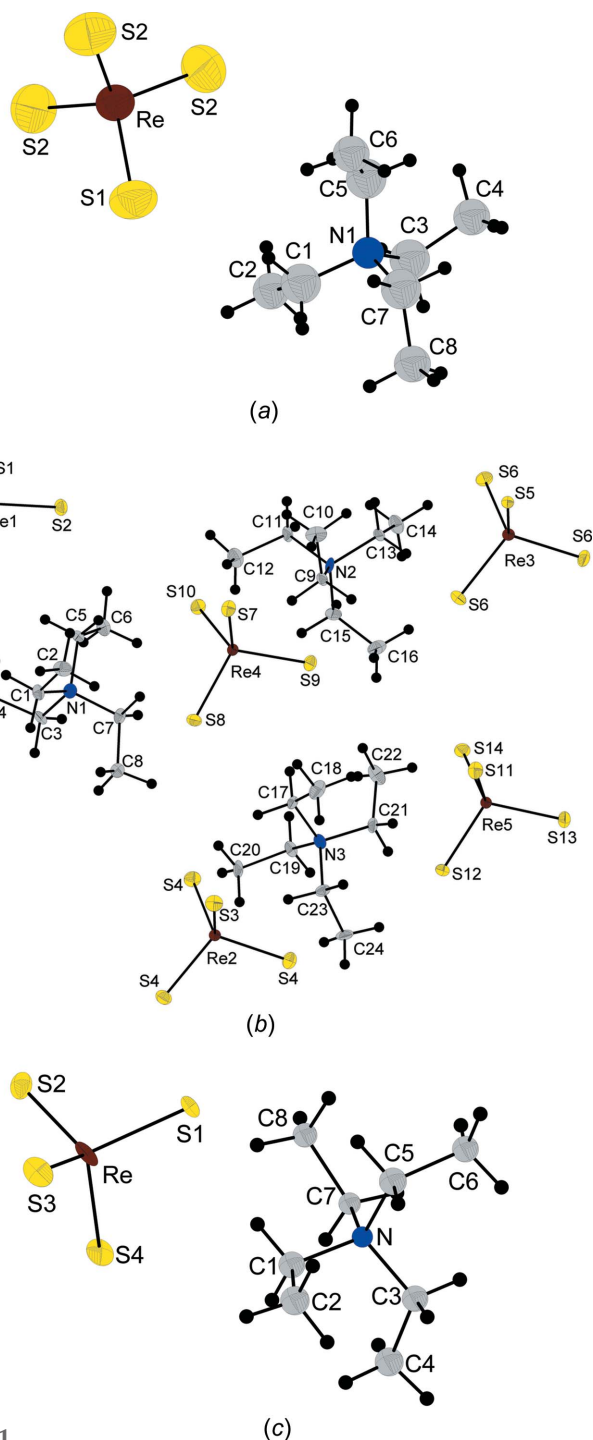
Figure 1
Displacement ellipsoid plots (50% probability level) of (a) **Ia** at 297 K, (b) **Ic** at 150 K and (c) **Ib** at 110 K.

−0.004 (7) and −0.007 (7). Therefore, twinning by inversion could be excluded. All tetrathioperrhenate anions (ReS$_4^-$) and tetraethylammonium cations are completely ordered (Fig. 1c).

3. Results and discussion

At 297 K, Et$_4$NReS$_4$ is isostructural with Et$_4$NFeCl$_4$ (Lutz *et al.*, 2014; Warnke *et al.*, 2010; Evans *et al.*, 1990; Navarro *et al.*,

Table 3
Crystallographic data for the high-temperature phase of several Et_4NMY4 compounds (M = B, Cl, Re, Fe, In and Tl; Y = O, F, S, Cl and Br).

Anion	$BF_4^{-,a}$	$ClO_4^{-,b}$	$ReS_4^{-,c}$	$FeCl_4^{-,d}$	$FeBrCl_3^{-,e}$	$InCl_4^{-,f}$	$TlCl_4^{-,g}$
Temperature (K)	373	393	297 (2)	290–295	293	r.t.[h]	297
Temperature range (K)	>342	>378.5	>285	>234.7	n.d.[i]	n.d.	>222
Space group	$Fm\bar{3}m$	$Fm\bar{3}m$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$	$P6_3mc$
Z	4	4	2	2	2	2	2
V/Z ($Å^3$)	317.3 (4)	329.1	376.42 (7)	383.7–385.7	388.4 (1)	397	394.7 (4)

Notes and references: (*a*) Matsumoto *et al.* (2014); (*b*) Ye *et al.* (2016); (*c*) this work; (*d*) Lutz *et al.* (2014), Warnke *et al.* (2010), Evans *et al.* (1990) and Navarro *et al.* (1988); (*e*) Evans *et al.* (1990); (*f*) Trotter *et al.* (1969); (*g*) Lenck *et al.* (1991); (*h*) r.t. = room temperature; (*i*) n.d. = not determined.

Table 4
Crystallographic data for the low-temperature phase of several Et_4NMY4 compounds (M = B, P, Cl, Mn, Re and Fe; Y = O, F, S and Cl).

Anion	$ClO_4^{-,a}$	$BF_4^{-,b}$	$MnO_4^{-,c}$	$PO_2F_2^{-,d}$	$ReO_3S^{-,e}$	$ReS_4^{-,f}$	$ReS_4^{-,f}$	$FeCl_4^{-,g}$	$FeCl_4^{-,h}$
Temperature (K)	110–173	298	293	110	293 (2)	149.9 (3)	109.9 (3)	110–170	230
Temperature range (K)	<378.5	<342	n.d.[i]	<323	n.d.	<285	metastable	<226.6	234.7–226.6
Apace group	Cc	Cc	$P2_1/c$	Cc	$P2_1/c$	$P2_1$	$P6_3$	$Pca2_1$	$P6_3$
Z	4	4	4	4	8	2	18	4	18
V/Z ($Å^3$)	291.3–294.5	294.5 (3)	307.7 (1)	311.39 (4)	316.7 (1)	360.0 (2)	363.05 (2)	363.77–367.75	376.86 (3)

Notes and references: (*a*) Ibers (1993), Kivikoski *et al.* (1995) and Ye *et al.* (2016); (*b*) Giuseppetti *et al.* (1994), Matsumoto *et al.* (2012) and Matsumoto *et al.* (2014); (*c*) Whang *et al.* (1991); (*d*) Matsumoto *et al.* (2012); (*e*) Partyka & Holm (2004); (*f*) this work; (*g*) Lutz *et al.* (2014) and Navarro *et al.* (1988); (*h*) Lutz *et al.* (2014) and Navarro *et al.* (1988); (*i*) n.d. = not determined.

1988), $Et_4NFeBrCl_3$ (Evans *et al.*, 1990), Et_4NInCl_4 (Trotter *et al.*, 1969) and Et_4NTlCl_4 (Lenck *et al.*, 1991). They crystallize in the space group $P6_3mc$. While the anion is ordered, the tetraethylammonium cation is disordered. The volume of the primitive cell grows in the following series $Et_4NBF_4 \simeq Et_4NClO_4 < Et_4NMnO_4 \simeq Et_4NPO_2F_2 \simeq Et_4NReOS_3 < Et_4NReS_4 < Et_4NFeCl_4 < Et_4NFeBrCl_3 < Et_4NTlCl_4 \simeq Et_4NInCl_4$. Accordingly, in the series Et_4NClO_4 (378.5 K) > Et_4NBF_4 (342 K) > $Et_4NPO_2F_2$ (323 K) > Et_4NReS_4 (285 K) > Et_4NFeCl_4 (234.7 K) > Et_4NTlCl_4 (222 K), the transition temperature to an ordered structure decreases (Tables 3 and 4).

While Et_4NFeCl_4 at 234.7 K undergoes a phase transition from $P6_3mc$ to $P6_3$ (Lutz *et al.*, 2014; Navarro *et al.*, 1988), a phase transition from $P6_3mc$ to $P2_1$ is observed for Et_4NReS_4 at 285 K. The $P6_3$ phase is metastable for Et_4NReS_4, while the $P2_1$ phase is not observed for Et_4NFeCl_4. An additional low-temperature phase of Et_4NFeCl_4 crystallizes in the space group $Pca2_1$ [226.6 (1)–2.93 (3) K] (Lutz *et al.*, 2014; Navarro *et al.*, 1988). This phase is not observed for Et_4NReS_4. While the high-temperature phases of the compounds from Table 3

Table 5
Intensity of the reflections with even and odd l (**Ia** and **Ic**) or k (**Ic**) from the .fcf file.

	F_{av}^2(odd)/F_{av}^2	F_{av}^2(even)/F_{av}^2	F_{av}^2(odd)/F_{av}^2(even)	Δ^a (Å)
Ia (obs)	0.082	1.737	0.047	0
Ia (calc)	0.080	1.740	0.046	0
Ib (obs)[b]	0.184	1.815	0.102	0.0573[c]
Ib (calc)	0.174	1.826	0.095	0.0573[c]
Ic (obs)	0.803	1.196	0.672	0.2720
Ic (calc)	0.796	1.203	0.662	0.2720

Notes: (*a*) Average displacement of the Re atoms from the threefold axis. (*b*) Reflections of **Ib** with h = 3n and k = 3m overlap with appropriate reflections of **Ic**. The reflections with h = 3n and k = 3m are on average 1.2 times too strong and were not used in the refinement. (*c*) Re1, Re2 and Re3 = 0 Å; Re4 = 0.0815 Å; Re5 = 0.0905 Å.

have the same structure, the low-temperature phases show different structures (Table 4). Tetraethylammonium salts with anions smaller than tetrathiorhenate crystallize at room temperature as the low-temperature phase of Et_4NReS_4. Whereas the tetraethylammonium cation in Et_4NBF_4, Et_4NClO_4, $Et_4NPO_2F_2$, Et_4NReS_4, Et_4NFeCl_4, $Et_4NFeBrCl_3$ and Et_4NTlCl_4 has the *tg–tg* conformation (*t* is *trans* and *g* is *gauche*), it has the *tt–tt* conformation in Et_4NReO_3S and Et_4NMnO_4 (Naudin *et al.*, 2000). Only the structures of Et_4NReO_3S, Et_4NMnO_4, Et_4NBF_4 (high-temperature phase) and Et_4NClO_4 (high-temperature phase) have an inversion centre. In these two compounds, the Et_4N^+ cation has a *tg–tg* conformation or is disordered.

At 297 K, Et_4NReS_4 crystallizes in the space group $P6_3mc$ (Tables 1 and 4). Because of the special position of the Re atom (2*a*, 3*m*.; Arnold, 1983), all reflections with $l = 2n + 1$ are much weaker than those with $l = 2n$ (Table 5). This could explain why Müller *et al.* (1986, 1987) found a smaller primitive cell [$P6mm$, a = 8.149 (2), c = 6.538 (1) Å, Z = 1]. They observed weak superstructural reflections, suggesting a doubling of the primitive cell [a = 8.149 (2), c = 13.076 (2) Å, Z = 2], which would be in good agreement with the one found here.

In **Ib** and **Ic**, the Re atom is displaced from the threefold axis. In **Ic**, reflections with $k = 2n + 1$ are as strong as the reflections with $k = 2n$, while for **Ib** (as also for **Ia**), reflections with $l = 2n + 1$ are much weaker than those with $l = 2n$ (Table 5).

Structurally, **Ib** is closer to **Ia** than to **Ic**. Therefore, **Ib** is also formed by rapid cooling of **Ia**, although **Ic** is thermodynamically more stable. The energy barrier for the conversion of **Ib** to **Ic** is relatively large, so that rapid conversion occurs only above 200 K.

In the known structures with ReS_4^-, the Re—S bond length is independent of the cation (Table 6). The S—Re—S angle in

Table 6
Re—S bond lengths (Å) and S—Re—S angles (°) for some compounds with the ReS_4^- anion.

Cation	Et_4N^+, **Ib**[a]	Et_4N^+, **Ic**[a]	Et_4N^+, **Ia**[a]	$Et_4N^{+,b}$	$Bu_4N^{+,c}$	$Ph_4P^{+,d}$
Temperature (K)	109.9 (3)	149.9 (3)	297 (2)	r.t.[e]	r.t.	r.t.
Re—S average	2.142 (2)	2.122 (10)	2.125 (4)	2.125 (4)	2.122 (6)	2.155 (30)
Re—S range	2.130–2.154	2.111–2.133	2.120–2.127	2.123–2.126	2.118–2.126	2.155–2.155
S—Re—S average	109.47 (9)	109.47 (71)	109.47 (17)	109.45 (11)	109.48 (84)	Not specified
S—Re—S range	109.06–109.95	108.01–110.61	109.33–109.61	109.4–109.5	107.4–112.8	Not specified

Notes and references: (a) this work; (b) Müller *et al.* (1987); (c) Do *et al.* (1985); (d) Diemann & Müller (1976); (e) r.t. = room temperature.

the ReS_4^- anion is very close to the tetrahedral value (109.47°). The Re—S bond length in ReO_3S^- is very similar to that in ReS_4^-. For ReO_3S^-, the following Re—S bond lengths are known: $RbReO_3S$ with 2.126 (6) Å (Krebs & Kindler, 1969) and Et_4NReO_3S with 2.128 (5) and 2.143 (5) Å (Partyka & Holm, 2004).

In this article, we were able to show that the unit cell of Et_4NReS_4 is larger at room temperature than previously thought (Müller *et al.*, 1986, 1987). In this structure, the Et_4N^+ cation is disordered, while the ReS_4^- anion is ordered. At 285 K, there is a phase transition to an ordered structure, where the space group changes from $P6_3mc$ to $P2_1$. The omission of the threefold axis and the mirror plane creates a twin with six components. In addition to this low-temperature phase, a further metastable phase was formed when **Ia** was cooled rapidly to 110–170 K. This phase crystallizes in the space group $P6_3$ with a nine times bigger unit cell forming an allotwin with **Ib**.

Acknowledgements

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Phase transition and structures of the twinned low-temperature phases of (Et$_4$N)[ReS$_4$]

Eduard Bernhardt and Regine Herbst-Irmer

Computing details

For all structures, data collection: *CrysAlis PRO* (Oxford Diffraction, 2016); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2016); data reduction: *CrysAlis PRO* (Oxford Diffraction, 2016); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015).

Tetraethylammonium tetrathiorhenate (Ia)

Crystal data

(C$_8$H$_{20}$N)[ReS$_4$]	D_x = 1.961 Mg m^{-3}
M_r = 444.69	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hexagonal, $P6_3mc$	Cell parameters from 687 reflections
a = 8.150 (2) Å	θ = 2.9–24.9°
c = 13.092 (3) Å	μ = 8.59 mm^{-1}
V = 753.1 (4) Å^3	T = 297 K
Z = 2	Prism, black
$F(000)$ = 428	0.32 × 0.03 × 0.03 mm

Data collection

Oxford Diffraction Gemini E Ultra diffractometer with an EOS CCD camera	T_{min} = 0.599, T_{max} = 0.829
	1804 measured reflections
Radiation source: fine-focus sealed tube Enhanced (Mo)	513 independent reflections
	392 reflections with $I > 2\sigma(I)$
Graphite monochromator	R_{int} = 0.029
Detector resolution: 16.2705 pixels mm^{-1}	θ_{max} = 26.7°, θ_{min} = 2.9°
ω scans	$h = -10 \rightarrow 5$
Absorption correction: analytical [CrysAlis PRO (Agilent, 2013), based on expressions derived by Clark & Reid (1995)]	$k = -7 \rightarrow 10$
	$l = -8 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.021	H-atom parameters constrained
$wR(F^2)$ = 0.048	$w = 1/[\sigma^2(F_o^2) + (0.018P)^2]$
S = 1.08	where $P = (F_o^2 + 2F_c^2)/3$
513 reflections	$(\Delta/\sigma)_{max} < 0.001$
44 parameters	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
34 restraints	$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Absolute structure: Refined as an inversion twin.

Absolute structure parameter: 0.14 (4)

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.

Refinement. Refined as a 2-component inversion twin.

Suitable single crystals of Et_4NReS_4 were attached to a goniometer head. The data collection was performed using an Oxford Diffraction Gemini E Ultra diffractometer with a 2K × 2K EOS CCD camera, a four-circle goniometer with κ geometry, a sealed-tube Mo radiation source, and an Oxford Instruments Cryojet cooling unit. Processing of the raw data, scaling of the diffraction data and the application of an empirical absorption correction were performed with the *CrysAlisPro* program (CrysAlis PRO, 2016). The structures were solved by direct methods and refined against F^2 (Sheldrick, 2015, 2008). The graphics were prepared with the program *Diamond* (Brandenburg, 2001). Full details of all structural data (CCDC-1971807 to CCDC-1971809) are presented in Section S of the Supporting Information File.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Re	0.0000	0.0000	0.0550 (2)	0.0597 (2)	
S1	0.0000	0.0000	0.2173 (4)	0.0829 (17)	
S2	−0.14196 (19)	0.14196 (19)	0.0010 (3)	0.0930 (8)	
N1	0.678 (4)	0.331 (3)	0.3103 (10)	0.041 (3)*	0.1667
C1	0.513 (4)	0.139 (3)	0.328 (2)	0.065 (5)*	0.1667
H1A	0.4031	0.1402	0.3009	0.078*	0.1667
H1B	0.4953	0.1250	0.4018	0.078*	0.1667
C2	0.506 (6)	−0.038 (3)	0.290 (3)	0.054 (5)*	0.1667
H2A	0.3881	−0.1463	0.3092	0.082*	0.1667
H2B	0.6092	−0.0478	0.3182	0.082*	0.1667
H2C	0.5163	−0.0325	0.2164	0.082*	0.1667
C3	0.850 (4)	0.314 (4)	0.293 (3)	0.065 (5)*	0.1667
H3A	0.8878	0.2857	0.3581	0.078*	0.1667
H3B	0.8150	0.2056	0.2488	0.078*	0.1667
C4	1.020 (5)	0.480 (6)	0.248 (3)	0.054 (5)*	0.1667
H4A	1.1202	0.4522	0.2402	0.082*	0.1667
H4B	1.0604	0.5882	0.2914	0.082*	0.1667
H4C	0.9873	0.5078	0.1817	0.082*	0.1667
C5	0.662 (5)	0.428 (5)	0.2172 (17)	0.065 (5)*	0.1667
H5A	0.7897	0.5192	0.1956	0.078*	0.1667
H5B	0.6071	0.3336	0.1637	0.078*	0.1667
C6	0.554 (6)	0.529 (6)	0.220 (3)	0.054 (5)*	0.1667
H6A	0.5582	0.5822	0.1543	0.082*	0.1667
H6B	0.6084	0.6278	0.2702	0.082*	0.1667
H6C	0.4247	0.4411	0.2380	0.082*	0.1667
C7	0.704 (7)	0.451 (3)	0.4029 (16)	0.065 (5)*	0.1667
H7A	0.5927	0.4641	0.4088	0.078*	0.1667
H7B	0.8110	0.5760	0.3900	0.078*	0.1667
C8	0.736 (3)	0.386 (6)	0.5047 (14)	0.054 (5)*	0.1667

H8A	0.7497	0.4756	0.5563	0.082*	0.1667
H8B	0.8484	0.3766	0.5019	0.082*	0.1667
H8C	0.6292	0.2642	0.5209	0.082*	0.1667

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re	0.0630 (3)	0.0630 (3)	0.0530 (3)	0.03152 (13)	0.000	0.000
S1	0.097 (3)	0.097 (3)	0.054 (3)	0.0486 (14)	0.000	0.000
S2	0.1049 (17)	0.1049 (17)	0.0908 (15)	0.069 (2)	−0.0080 (11)	0.0080 (11)

Geometric parameters (Å, º)

Re—S1	2.124 (5)	C3—H3B	0.9700
Re—S2^i	2.125 (3)	C4—H4A	0.9600
Re—S2^{ii}	2.125 (3)	C4—H4B	0.9600
Re—S2	2.125 (3)	C4—H4C	0.9600
N1—C1	1.485 (19)	C5—C6	1.47 (3)
N1—C5	1.496 (19)	C5—H5A	0.9700
N1—C3	1.496 (19)	C5—H5B	0.9700
N1—C7	1.502 (18)	C6—H6A	0.9600
C1—C2	1.51 (2)	C6—H6B	0.9600
C1—H1A	0.9700	C6—H6C	0.9600
C1—H1B	0.9700	C7—C8	1.50 (2)
C2—H2A	0.9600	C7—H7A	0.9700
C2—H2B	0.9600	C7—H7B	0.9700
C2—H2C	0.9600	C8—H8A	0.9600
C3—C4	1.49 (3)	C8—H8B	0.9600
C3—H3A	0.9700	C8—H8C	0.9600
S1—Re—S2^i	109.44 (14)	C3—C4—H4A	109.5
S1—Re—S2^{ii}	109.44 (14)	C3—C4—H4B	109.5
S2^i—Re—S2^{ii}	109.51 (14)	H4A—C4—H4B	109.5
S1—Re—S2	109.44 (14)	C3—C4—H4C	109.5
S2^i—Re—S2	109.50 (14)	H4A—C4—H4C	109.5
S2^{ii}—Re—S2	109.50 (14)	H4B—C4—H4C	109.5
C1—N1—C5	114 (2)	C6—C5—N1	121 (2)
C1—N1—C3	108.9 (18)	C6—C5—H5A	107.2
C5—N1—C3	105.2 (19)	N1—C5—H5A	107.2
C1—N1—C7	108.2 (18)	C6—C5—H5B	107.2
C5—N1—C7	109.6 (17)	N1—C5—H5B	107.2
C3—N1—C7	110 (3)	H5A—C5—H5B	106.8
N1—C1—C2	122 (2)	C5—C6—H6A	109.5
N1—C1—H1A	106.7	C5—C6—H6B	109.5
C2—C1—H1A	106.7	H6A—C6—H6B	109.5
N1—C1—H1B	106.7	C5—C6—H6C	109.5
C2—C1—H1B	106.7	H6A—C6—H6C	109.5
H1A—C1—H1B	106.6	H6B—C6—H6C	109.5

C1—C2—H2A	109.5	N1—C7—C8	119 (2)
C1—C2—H2B	109.5	N1—C7—H7A	107.6
H2A—C2—H2B	109.5	C8—C7—H7A	107.6
C1—C2—H2C	109.5	N1—C7—H7B	107.6
H2A—C2—H2C	109.5	C8—C7—H7B	107.6
H2B—C2—H2C	109.5	H7A—C7—H7B	107.1
C4—C3—N1	117 (2)	C7—C8—H8A	109.5
C4—C3—H3A	108.0	C7—C8—H8B	109.5
N1—C3—H3A	108.0	H8A—C8—H8B	109.5
C4—C3—H3B	108.0	C7—C8—H8C	109.5
N1—C3—H3B	108.0	H8A—C8—H8C	109.5
H3A—C3—H3B	107.2	H8B—C8—H8C	109.5

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

Tetraethylammonium tetrathiorhenate (Ib)

Crystal data

$(C_8H_{20}N)[ReS_4]$
$M_r = 444.69$
Hexagonal, $P6_3$
$a = 24.170$ (3) Å
$c = 12.916$ (2) Å
$V = 6534.5$ (19) Å^3
$Z = 18$
$F(000) = 3852$

$D_x = 2.034$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 16453 reflections
$\theta = 2.9–29.3°$
$\mu = 8.91$ mm^{-1}
$T = 110$ K
Prism, black
$0.24 \times 0.21 \times 0.16$ mm

Data collection

Oxford Diffraction Gemini E Ultra
   diffractometer with an EOS CCD camera
Radiation source: fine-focus sealed tube
   Enhanced (Mo)
Graphite monochromator
Detector resolution: 16.2705 pixels mm^{-1}
ω scans
Absorption correction: analytical
   [CrysAlis PRO (Agilent, 2013), based on
   expressions derived by Clark & Reid (1995)]

$T_{min} = 0.253$, $T_{max} = 0.351$
44958 measured reflections
9707 independent reflections
8807 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 29.7°$, $\theta_{min} = 1.9°$
$h = -32 \rightarrow 29$
$k = -30 \rightarrow 27$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.048$
$S = 1.05$
9707 reflections
380 parameters
1 restraint
Hydrogen site location: inferred from
   neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.008P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.87$ e Å^{-3}
$\Delta\rho_{min} = -1.08$ e Å^{-3}
Absolute structure: Twinning involves
   inversion, so Flack parameter cannot be
   determined

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.

Refinement. Refined as a 2-component inversion twin.

Suitable single crystals of Et_4NReS_4 were attached to a goniometer head. The data collection was performed using an Oxford Diffraction Gemini E Ultra diffractometer with a 2K × 2K EOS CCD camera, a four-circle goniometer with κ geometry, a sealed-tube Mo radiation source, and an Oxford Instruments Cryojet cooling unit. Processing of the raw data, scaling of the diffraction data and the application of an empirical absorption correction were performed with the *CrysAlisPro* program (CrysAlis PRO, 2016). The structures were solved by direct methods and refined against F^2 (Sheldrick, 2015, 2008). The graphics were prepared with the program *Diamond* (Brandenburg, 2001). Full details of all structural data (CCDC-1971807 to CCDC-1971809) are presented in Section S of the Supporting Information File.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Re1	0.000000	0.000000	0.35220 (11)	0.0095 (2)
S1	0.000000	0.000000	0.5175 (4)	0.0158 (12)
S2	0.03466 (11)	0.09562 (11)	0.2979 (2)	0.0170 (5)
Re2	0.666667	0.333333	0.35177 (11)	0.0096 (2)
S3	0.666667	0.333333	0.5165 (4)	0.0165 (11)
S4	0.72698 (11)	0.42896 (12)	0.2975 (2)	0.0178 (5)
Re3	0.333333	0.666667	0.35284 (11)	0.0097 (2)
S5	0.333333	0.666667	0.5197 (4)	0.0107 (11)
S6	0.39202 (11)	0.76280 (12)	0.2985 (2)	0.0171 (5)
Re4	0.33152 (2)	0.32944 (2)	0.39300 (2)	0.00888 (14)
S7	0.31787 (9)	0.32427 (9)	0.55692 (15)	0.0152 (4)
S8	0.38743 (10)	0.28632 (10)	0.35143 (18)	0.0150 (5)
S9	0.38027 (11)	0.42763 (11)	0.34619 (18)	0.0154 (5)
S10	0.24045 (10)	0.27951 (12)	0.3185 (2)	0.0159 (5)
Re5	0.66238 (2)	0.66500 (2)	0.38567 (2)	0.0106 (2)
S11	0.65647 (9)	0.65264 (10)	0.55018 (16)	0.0178 (5)
S12	0.70584 (12)	0.61460 (11)	0.31983 (18)	0.0151 (5)
S13	0.71863 (11)	0.76468 (10)	0.3498 (2)	0.0160 (5)
S14	0.56841 (11)	0.62819 (12)	0.32167 (18)	0.0165 (5)
N1	0.2288 (5)	0.1209 (4)	0.1357 (17)	0.016 (2)
C1	0.2347 (4)	0.0831 (4)	0.2256 (5)	0.0139 (16)
H1A	0.195518	0.040614	0.228117	0.017*
H1B	0.271116	0.076230	0.211697	0.017*
C2	0.2444 (6)	0.1145 (4)	0.3303 (8)	0.020 (2)
H2A	0.247669	0.087276	0.383348	0.031*
H2B	0.283761	0.156106	0.329500	0.031*
H2C	0.208025	0.120425	0.345950	0.031*
C3	0.2216 (3)	0.0835 (3)	0.0367 (5)	0.0129 (15)
H3A	0.220731	0.109107	−0.022482	0.015*
H3B	0.260166	0.079511	0.028873	0.015*
C4	0.1635 (4)	0.0173 (3)	0.0288 (5)	0.020 (2)
H4A	0.164110	−0.001845	−0.037826	0.029*

H4B	0.164196	−0.009433	0.085252	0.029*
H4C	0.124613	0.020274	0.033705	0.029*
C5	0.1699 (3)	0.1264 (4)	0.1529 (6)	0.0149 (17)
H5A	0.133393	0.083134	0.166333	0.018*
H5B	0.176498	0.152166	0.216189	0.018*
C6	0.1520 (4)	0.1554 (4)	0.0670 (5)	0.0205 (18)
H6A	0.113364	0.156707	0.086097	0.031*
H6B	0.186976	0.198975	0.054225	0.031*
H6C	0.143741	0.129734	0.004219	0.031*
C7	0.2858 (3)	0.1860 (3)	0.1261 (6)	0.0127 (16)
H7A	0.287911	0.211108	0.187997	0.015*
H7B	0.279841	0.207276	0.065088	0.015*
C8	0.3494 (5)	0.1881 (4)	0.1149 (7)	0.021 (2)
H8A	0.383880	0.232598	0.109143	0.031*
H8B	0.356776	0.168417	0.175826	0.031*
H8C	0.348687	0.164576	0.052619	0.031*
N2	0.2191 (3)	0.4378 (5)	0.1385 (18)	0.015 (3)
C9	0.2538 (4)	0.4319 (3)	0.2279 (5)	0.0135 (16)
H9A	0.296381	0.470942	0.231879	0.016*
H9B	0.260564	0.395301	0.215868	0.016*
C10	0.2202 (4)	0.4225 (6)	0.3320 (8)	0.021 (2)
H10A	0.246203	0.419085	0.386971	0.032*
H10B	0.214278	0.459133	0.345867	0.032*
H10C	0.178397	0.383357	0.329828	0.032*
C11	0.1531 (3)	0.3811 (3)	0.1254 (6)	0.0160 (17)
H11A	0.133278	0.388131	0.063544	0.019*
H11B	0.127056	0.378589	0.186186	0.019*
C12	0.1506 (4)	0.3168 (5)	0.1135 (8)	0.022 (2)
H12A	0.106143	0.282752	0.105395	0.033*
H12B	0.175213	0.318095	0.052290	0.033*
H12C	0.168977	0.308533	0.175190	0.033*
C13	0.2127 (3)	0.4978 (3)	0.1536 (5)	0.0131 (16)
H13A	0.184222	0.490526	0.213448	0.016*
H13B	0.255231	0.534329	0.170945	0.016*
C14	0.1863 (4)	0.5160 (4)	0.0596 (6)	0.0201 (17)
H14A	0.183867	0.554361	0.075788	0.030*
H14B	0.214761	0.524662	0.000237	0.030*
H14C	0.143610	0.480770	0.042825	0.030*
C15	0.2578 (3)	0.4447 (3)	0.0404 (5)	0.0172 (16)
H15A	0.262081	0.406278	0.033457	0.021*
H15B	0.233415	0.446039	−0.020227	0.021*
C16	0.3235 (4)	0.5029 (4)	0.0376 (6)	0.023 (2)
H16A	0.344677	0.503511	−0.027391	0.034*
H16B	0.319934	0.541502	0.042338	0.034*
H16C	0.348662	0.501657	0.096135	0.034*
N3	0.5567 (3)	0.4520 (4)	0.1362 (16)	0.013 (3)
C17	0.5148 (3)	0.4158 (3)	0.2259 (5)	0.0132 (15)
H17A	0.511407	0.373309	0.229175	0.016*

H17B	0.471441	0.408995	0.213221	0.016*
C18	0.5382 (4)	0.4486 (4)	0.3301 (8)	0.023 (2)
H18A	0.508369	0.422111	0.384477	0.034*
H18B	0.580622	0.454563	0.344556	0.034*
H18C	0.540591	0.490307	0.328575	0.034*
C19	0.5261 (3)	0.4136 (3)	0.0387 (5)	0.0136 (15)
H19A	0.482758	0.407899	0.031716	0.016*
H19B	0.551399	0.438524	−0.021869	0.016*
C20	0.5207 (4)	0.3485 (3)	0.0357 (6)	0.0176 (19)
H20A	0.500567	0.327002	−0.029382	0.026*
H20B	0.563461	0.353448	0.040443	0.026*
H20C	0.494689	0.322765	0.094130	0.026*
C21	0.5629 (3)	0.5169 (3)	0.1230 (6)	0.0153 (17)
H21A	0.588891	0.537152	0.060404	0.018*
H21B	0.586552	0.543683	0.183095	0.018*
C22	0.5000 (4)	0.5170 (4)	0.1129 (7)	0.021 (2)
H22A	0.508879	0.560968	0.104620	0.031*
H22B	0.476566	0.491726	0.052262	0.031*
H22C	0.474221	0.498273	0.175262	0.031*
C23	0.6234 (3)	0.4607 (3)	0.1529 (5)	0.0138 (16)
H23A	0.642488	0.487591	0.215039	0.017*
H23B	0.618705	0.418332	0.167444	0.017*
C24	0.6693 (4)	0.4905 (4)	0.0638 (5)	0.0180 (17)
H24A	0.710386	0.494019	0.081621	0.027*
H24B	0.651791	0.463676	0.002054	0.027*
H24C	0.675632	0.533108	0.049767	0.027*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.0105 (3)	0.0105 (3)	0.0075 (5)	0.00524 (13)	0.000	0.000
S1	0.0201 (18)	0.0201 (18)	0.007 (2)	0.0101 (9)	0.000	0.000
S2	0.0194 (12)	0.0124 (11)	0.0195 (11)	0.0082 (10)	0.0002 (10)	0.0028 (9)
Re2	0.0102 (3)	0.0102 (3)	0.0084 (6)	0.00512 (14)	0.000	0.000
S3	0.0224 (18)	0.0224 (18)	0.005 (2)	0.0112 (9)	0.000	0.000
S4	0.0187 (12)	0.0148 (11)	0.0174 (11)	0.0065 (10)	0.0010 (10)	0.0034 (9)
Re3	0.0115 (3)	0.0115 (3)	0.0063 (6)	0.00573 (14)	0.000	0.000
S5	0.0113 (16)	0.0113 (16)	0.010 (3)	0.0056 (8)	0.000	0.000
S6	0.0178 (11)	0.0112 (11)	0.0185 (12)	0.0042 (9)	0.0024 (10)	0.0032 (9)
Re4	0.00993 (19)	0.0092 (2)	0.0069 (3)	0.00435 (15)	−0.00001 (13)	0.00042 (19)
S7	0.0193 (10)	0.0147 (10)	0.0090 (8)	0.0065 (8)	0.0004 (8)	0.0011 (7)
S8	0.0135 (10)	0.0169 (10)	0.0167 (11)	0.0093 (8)	0.0016 (9)	−0.0010 (9)
S9	0.0169 (11)	0.0127 (9)	0.0150 (10)	0.0062 (9)	0.0013 (9)	0.0041 (8)
S10	0.0124 (10)	0.0159 (12)	0.0176 (11)	0.0058 (9)	−0.0044 (8)	−0.0024 (9)
Re5	0.0095 (2)	0.0093 (2)	0.0129 (6)	0.00455 (15)	0.00000 (18)	−0.00072 (13)
S11	0.0218 (12)	0.0161 (11)	0.0138 (9)	0.0082 (8)	0.0000 (8)	0.0005 (8)
S12	0.0147 (11)	0.0146 (11)	0.0182 (11)	0.0089 (9)	0.0044 (9)	0.0007 (9)
S13	0.0167 (11)	0.0111 (9)	0.0189 (13)	0.0059 (9)	−0.0014 (9)	0.0011 (8)

S14	0.0118 (10)	0.0179 (12)	0.0197 (11)	0.0074 (9)	−0.0026 (8)	−0.0029 (9)
N1	0.016 (6)	0.014 (3)	0.015 (5)	0.006 (3)	0.000 (4)	−0.001 (6)
C1	0.019 (5)	0.011 (4)	0.013 (4)	0.008 (4)	0.000 (3)	0.001 (3)
C2	0.023 (6)	0.027 (5)	0.018 (5)	0.017 (4)	0.003 (4)	0.006 (3)
C3	0.016 (4)	0.012 (4)	0.014 (4)	0.010 (3)	−0.001 (3)	−0.004 (3)
C4	0.020 (5)	0.023 (5)	0.020 (4)	0.015 (4)	−0.001 (3)	−0.004 (3)
C5	0.013 (4)	0.011 (4)	0.023 (5)	0.008 (4)	0.003 (3)	0.000 (3)
C6	0.023 (5)	0.015 (4)	0.027 (4)	0.011 (4)	0.002 (4)	0.002 (4)
C7	0.014 (4)	0.010 (4)	0.010 (4)	0.002 (3)	−0.003 (3)	−0.004 (3)
C8	0.014 (5)	0.014 (5)	0.033 (5)	0.007 (4)	0.003 (4)	0.002 (4)
N2	0.012 (5)	0.005 (5)	0.021 (8)	0.000 (3)	0.000 (4)	0.001 (5)
C9	0.009 (4)	0.009 (4)	0.022 (4)	0.005 (3)	−0.004 (3)	−0.006 (3)
C10	0.020 (5)	0.033 (6)	0.012 (5)	0.014 (4)	−0.001 (3)	0.002 (4)
C11	0.013 (4)	0.008 (4)	0.024 (4)	0.003 (3)	−0.006 (3)	−0.008 (3)
C12	0.023 (5)	0.019 (6)	0.024 (6)	0.011 (4)	−0.008 (4)	−0.005 (4)
C13	0.015 (4)	0.010 (4)	0.018 (4)	0.009 (3)	0.004 (3)	0.004 (3)
C14	0.024 (5)	0.018 (4)	0.022 (4)	0.014 (4)	−0.007 (4)	−0.002 (4)
C15	0.018 (4)	0.020 (4)	0.015 (4)	0.010 (3)	0.006 (3)	−0.001 (3)
C16	0.016 (4)	0.025 (5)	0.023 (4)	0.007 (4)	0.005 (3)	0.002 (4)
N3	0.016 (4)	0.012 (4)	0.012 (6)	0.008 (4)	−0.003 (3)	−0.004 (5)
C17	0.010 (4)	0.009 (4)	0.018 (4)	0.003 (3)	0.003 (3)	0.003 (3)
C18	0.022 (5)	0.019 (5)	0.019 (6)	0.004 (4)	0.003 (4)	0.004 (3)
C19	0.014 (4)	0.012 (3)	0.015 (4)	0.007 (3)	−0.009 (3)	−0.008 (3)
C20	0.017 (4)	0.007 (4)	0.024 (4)	0.002 (3)	−0.004 (3)	−0.006 (3)
C21	0.014 (4)	0.008 (4)	0.023 (5)	0.005 (3)	0.001 (3)	0.004 (3)
C22	0.034 (5)	0.023 (5)	0.014 (5)	0.021 (4)	−0.006 (3)	−0.003 (4)
C23	0.008 (4)	0.016 (4)	0.016 (4)	0.004 (3)	−0.001 (3)	−0.002 (3)
C24	0.013 (4)	0.023 (4)	0.019 (4)	0.010 (4)	0.010 (4)	0.009 (4)

Geometric parameters (Å, º)

Re1—S1	2.135 (5)	C9—C10	1.528 (11)
Re1—S2	2.144 (2)	C9—H9A	0.9900
Re1—S2[i]	2.144 (2)	C9—H9B	0.9900
Re1—S2[ii]	2.144 (2)	C10—H10A	0.9800
Re2—S3	2.128 (5)	C10—H10B	0.9800
Re2—S4[iii]	2.142 (2)	C10—H10C	0.9800
Re2—S4[iv]	2.142 (2)	C11—C12	1.531 (11)
Re2—S4	2.142 (2)	C11—H11A	0.9900
Re3—S6[v]	2.146 (2)	C11—H11B	0.9900
Re3—S6	2.146 (2)	C12—H12A	0.9800
Re3—S6[vi]	2.146 (2)	C12—H12B	0.9800
Re3—S5	2.155 (5)	C12—H12C	0.9800
Re4—S7	2.137 (2)	C13—C14	1.534 (10)
Re4—S10	2.138 (2)	C13—H13A	0.9900
Re4—S9	2.142 (2)	C13—H13B	0.9900
Re4—S8	2.147 (2)	C14—H14A	0.9800
Re5—S11	2.141 (2)	C14—H14B	0.9800

Re5—S12	2.142 (2)	C14—H14C	0.9800
Re5—S13	2.143 (2)	C15—C16	1.506 (10)
Re5—S14	2.148 (2)	C15—H15A	0.9900
N1—C7	1.490 (11)	C15—H15B	0.9900
N1—C5	1.513 (11)	C16—H16A	0.9800
N1—C3	1.52 (2)	C16—H16B	0.9800
N1—C1	1.528 (18)	C16—H16C	0.9800
C1—C2	1.510 (11)	N3—C17	1.499 (18)
C1—H1A	0.9900	N3—C21	1.508 (12)
C1—H1B	0.9900	N3—C19	1.520 (18)
C2—H2A	0.9800	N3—C23	1.533 (10)
C2—H2B	0.9800	C17—C18	1.520 (11)
C2—H2C	0.9800	C17—H17A	0.9900
C3—C4	1.516 (10)	C17—H17B	0.9900
C3—H3A	0.9900	C18—H18A	0.9800
C3—H3B	0.9900	C18—H18B	0.9800
C4—H4A	0.9800	C18—H18C	0.9800
C4—H4B	0.9800	C19—C20	1.514 (9)
C4—H4C	0.9800	C19—H19A	0.9900
C5—C6	1.488 (10)	C19—H19B	0.9900
C5—H5A	0.9900	C20—H20A	0.9800
C5—H5B	0.9900	C20—H20B	0.9800
C6—H6A	0.9800	C20—H20C	0.9800
C6—H6B	0.9800	C21—C22	1.526 (11)
C6—H6C	0.9800	C21—H21A	0.9900
C7—C8	1.519 (11)	C21—H21B	0.9900
C7—H7A	0.9900	C22—H22A	0.9800
C7—H7B	0.9900	C22—H22B	0.9800
C8—H8A	0.9800	C22—H22C	0.9800
C8—H8B	0.9800	C23—C24	1.508 (9)
C8—H8C	0.9800	C23—H23A	0.9900
N2—C9	1.48 (2)	C23—H23B	0.9900
N2—C11	1.505 (10)	C24—H24A	0.9800
N2—C15	1.53 (2)	C24—H24B	0.9800
N2—C13	1.545 (11)	C24—H24C	0.9800
S1—Re1—S2	109.09 (8)	C9—C10—H10A	109.5
S1—Re1—S2ⁱ	109.09 (8)	C9—C10—H10B	109.5
S2—Re1—S2ⁱ	109.85 (8)	H10A—C10—H10B	109.5
S1—Re1—S2ⁱⁱ	109.09 (8)	C9—C10—H10C	109.5
S2—Re1—S2ⁱⁱ	109.85 (8)	H10A—C10—H10C	109.5
S2ⁱ—Re1—S2ⁱⁱ	109.85 (8)	H10B—C10—H10C	109.5
S3—Re2—S4ⁱⁱⁱ	109.10 (8)	N2—C11—C12	115.0 (6)
S3—Re2—S4ⁱᵛ	109.10 (8)	N2—C11—H11A	108.5
S4ⁱⁱⁱ—Re2—S4ⁱᵛ	109.84 (8)	C12—C11—H11A	108.5
S3—Re2—S4	109.10 (8)	N2—C11—H11B	108.5
S4ⁱⁱⁱ—Re2—S4	109.84 (8)	C12—C11—H11B	108.5
S4ⁱᵛ—Re2—S4	109.84 (7)	H11A—C11—H11B	107.5

S6ᵛ—Re3—S6	109.87 (7)	C11—C12—H12A	109.5
S6ᵛ—Re3—S6ᵛⁱ	109.87 (7)	C11—C12—H12B	109.5
S6—Re3—S6ᵛⁱ	109.87 (7)	H12A—C12—H12B	109.5
S6ᵛ—Re3—S5	109.07 (7)	C11—C12—H12C	109.5
S6—Re3—S5	109.07 (7)	H12A—C12—H12C	109.5
S6ᵛⁱ—Re3—S5	109.07 (7)	H12B—C12—H12C	109.5
S7—Re4—S10	109.13 (8)	C14—C13—N2	114.9 (10)
S7—Re4—S9	109.13 (8)	C14—C13—H13A	108.5
S10—Re4—S9	109.81 (9)	N2—C13—H13A	108.5
S7—Re4—S8	109.61 (8)	C14—C13—H13B	108.5
S10—Re4—S8	109.49 (10)	N2—C13—H13B	108.5
S9—Re4—S8	109.64 (8)	H13A—C13—H13B	107.5
S11—Re5—S12	109.40 (7)	C13—C14—H14A	109.5
S11—Re5—S13	109.38 (9)	C13—C14—H14B	109.5
S12—Re5—S13	109.74 (9)	H14A—C14—H14B	109.5
S11—Re5—S14	109.96 (8)	C13—C14—H14C	109.5
S12—Re5—S14	109.23 (9)	H14A—C14—H14C	109.5
S13—Re5—S14	109.13 (9)	H14B—C14—H14C	109.5
C7—N1—C5	109.5 (6)	C16—C15—N2	115.0 (7)
C7—N1—C3	109.1 (12)	C16—C15—H15A	108.5
C5—N1—C3	110.0 (10)	N2—C15—H15A	108.5
C7—N1—C1	112.4 (11)	C16—C15—H15B	108.5
C5—N1—C1	108.3 (12)	N2—C15—H15B	108.5
C3—N1—C1	107.4 (5)	H15A—C15—H15B	107.5
C2—C1—N1	114.7 (8)	C15—C16—H16A	109.5
C2—C1—H1A	108.6	C15—C16—H16B	109.5
N1—C1—H1A	108.6	H16A—C16—H16B	109.5
C2—C1—H1B	108.6	C15—C16—H16C	109.5
N1—C1—H1B	108.6	H16A—C16—H16C	109.5
H1A—C1—H1B	107.6	H16B—C16—H16C	109.5
C1—C2—H2A	109.5	C17—N3—C21	112.4 (10)
C1—C2—H2B	109.5	C17—N3—C19	107.6 (5)
H2A—C2—H2B	109.5	C21—N3—C19	107.8 (12)
C1—C2—H2C	109.5	C17—N3—C23	109.2 (12)
H2A—C2—H2C	109.5	C21—N3—C23	108.9 (5)
H2B—C2—H2C	109.5	C19—N3—C23	110.9 (10)
C4—C3—N1	117.0 (7)	N3—C17—C18	114.4 (7)
C4—C3—H3A	108.0	N3—C17—H17A	108.7
N1—C3—H3A	108.0	C18—C17—H17A	108.7
C4—C3—H3B	108.0	N3—C17—H17B	108.7
N1—C3—H3B	108.0	C18—C17—H17B	108.7
H3A—C3—H3B	107.3	H17A—C17—H17B	107.6
C3—C4—H4A	109.5	C17—C18—H18A	109.5
C3—C4—H4B	109.5	C17—C18—H18B	109.5
H4A—C4—H4B	109.5	H18A—C18—H18B	109.5
C3—C4—H4C	109.5	C17—C18—H18C	109.5
H4A—C4—H4C	109.5	H18A—C18—H18C	109.5
H4B—C4—H4C	109.5	H18B—C18—H18C	109.5

C6—C5—N1	116.1 (10)	C20—C19—N3	114.8 (7)
C6—C5—H5A	108.3	C20—C19—H19A	108.6
N1—C5—H5A	108.3	N3—C19—H19A	108.6
C6—C5—H5B	108.3	C20—C19—H19B	108.6
N1—C5—H5B	108.3	N3—C19—H19B	108.6
H5A—C5—H5B	107.4	H19A—C19—H19B	107.6
C5—C6—H6A	109.5	C19—C20—H20A	109.5
C5—C6—H6B	109.5	C19—C20—H20B	109.5
H6A—C6—H6B	109.5	H20A—C20—H20B	109.5
C5—C6—H6C	109.5	C19—C20—H20C	109.5
H6A—C6—H6C	109.5	H20A—C20—H20C	109.5
H6B—C6—H6C	109.5	H20B—C20—H20C	109.5
N1—C7—C8	115.4 (6)	N3—C21—C22	115.5 (6)
N1—C7—H7A	108.4	N3—C21—H21A	108.4
C8—C7—H7A	108.4	C22—C21—H21A	108.4
N1—C7—H7B	108.4	N3—C21—H21B	108.4
C8—C7—H7B	108.4	C22—C21—H21B	108.4
H7A—C7—H7B	107.5	H21A—C21—H21B	107.5
C7—C8—H8A	109.5	C21—C22—H22A	109.5
C7—C8—H8B	109.5	C21—C22—H22B	109.5
H8A—C8—H8B	109.5	H22A—C22—H22B	109.5
C7—C8—H8C	109.5	C21—C22—H22C	109.5
H8A—C8—H8C	109.5	H22A—C22—H22C	109.5
H8B—C8—H8C	109.5	H22B—C22—H22C	109.5
C9—N2—C11	113.2 (12)	C24—C23—N3	115.5 (9)
C9—N2—C15	108.2 (4)	C24—C23—H23A	108.4
C11—N2—C15	108.4 (13)	N3—C23—H23A	108.4
C9—N2—C13	108.7 (12)	C24—C23—H23B	108.4
C11—N2—C13	108.2 (4)	N3—C23—H23B	108.4
C15—N2—C13	110.1 (11)	H23A—C23—H23B	107.5
N2—C9—C10	114.6 (8)	C23—C24—H24A	109.5
N2—C9—H9A	108.6	C23—C24—H24B	109.5
C10—C9—H9A	108.6	H24A—C24—H24B	109.5
N2—C9—H9B	108.6	C23—C24—H24C	109.5
C10—C9—H9B	108.6	H24A—C24—H24C	109.5
H9A—C9—H9B	107.6	H24B—C24—H24C	109.5

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

Tetraethylammonium tetrathiorhenate (Ic)

Crystal data

(C₈H₂₀N)[ReS₄]	$V = 720.0\ (3)$ Å³
$M_r = 444.69$	$Z = 2$
Monoclinic, $P2_1$	$F(000) = 428$
$a = 7.900\ (2)$ Å	$D_x = 2.051$ Mg m⁻³
$b = 12.842\ (3)$ Å	Mo *Kα* radiation, $\lambda = 0.71073$ Å
$c = 8.118\ (2)$ Å	Cell parameters from 3279 reflections
$\beta = 119.04\ (2)°$	$\theta = 2.9–29.5°$

$\mu = 8.99$ mm^{-1}
$T = 150$ K

Prism, black
0.24 × 0.20 × 0.17 mm

Data collection

Oxford Diffraction Gemini E Ultra diffractometer with an EOS CCD camera	$T_{min} = 0.241$, $T_{max} = 0.336$
Radiation source: fine-focus sealed tube Enhanced (Mo)	4476 measured reflections
	2814 independent reflections
	2808 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.053$
Detector resolution: 16.2705 pixels mm^{-1}	$\theta_{max} = 29.3°$, $\theta_{min} = 3.3°$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: analytical [CrysAlis PRO (Agilent, 2013), based on expressions derived by Clark & Reid (1995)]	$k = -15 \rightarrow 16$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.138$
$S = 1.09$
2814 reflections
87 parameters
89 restraints
Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0596P)^2 + 29.5424P]$
 where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 2.01$ e Å^{-3}
$\Delta\rho_{min} = -4.80$ e Å^{-3}
Absolute structure: Flack x determined using 1080 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.105 (18)

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.

Refinement. Refined as a 6-component twin.
Suitable single crystals of Et$_4$NReS$_4$ were attached to a goniometer head. The data collection was performed using an Oxford Diffraction Gemini E Ultra diffractometer with a 2K × 2K EOS CCD camera, a four-circle goniometer with κ geometry, a sealed-tube Mo radiation source, and an Oxford Instruments Cryojet cooling unit. Processing of the raw data, scaling of the diffraction data and the application of an empirical absorption correction were performed with the *CrysAlisPro* program (CrysAlis PRO, 2016). The structures were solved by direct methods and refined against F^2 (Sheldrick, 2015, 2008). The graphics were prepared with the program *Diamond* (Brandenburg, 2001). Full details of all structural data (CCDC-1971807 to CCDC-1971809) are presented in Section S of the Supporting Information File.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Re	0.0222 (5)	0.25452 (19)	0.03784 (19)	0.0174 (3)
S1	0.0542 (18)	0.4194 (5)	0.0361 (16)	0.023 (3)
S2	−0.105 (2)	0.1961 (8)	−0.2401 (14)	0.022 (2)
S3	−0.150 (2)	0.2166 (9)	0.163 (2)	0.026 (3)
S4	0.3036 (17)	0.1879 (9)	0.194 (2)	0.030 (3)
N	0.680 (3)	0.5128 (17)	0.326 (3)	0.016 (6)*
C1	0.595 (6)	0.417 (2)	0.366 (5)	0.025 (9)*
H1A	0.682470	0.357262	0.384336	0.030*
H1B	0.469486	0.401274	0.253227	0.030*

C2	0.562 (8)	0.422 (4)	0.537 (7)	0.030 (11)*
H2A	0.507365	0.356325	0.550356	0.045*
H2B	0.685905	0.435040	0.651499	0.045*
H2C	0.472238	0.479193	0.519969	0.045*
C3	0.878 (5)	0.535 (3)	0.492 (5)	0.025 (9)*
H3A	0.860836	0.555189	0.600623	0.029*
H3B	0.932921	0.596495	0.459715	0.029*
C4	1.025 (7)	0.447 (3)	0.552 (7)	0.029 (10)*
H4A	1.147093	0.468969	0.659847	0.044*
H4B	0.974470	0.386098	0.588604	0.044*
H4C	1.046759	0.427522	0.447296	0.044*
C5	0.546 (5)	0.604 (2)	0.292 (6)	0.027 (9)*
H5A	0.527783	0.612571	0.403188	0.033*
H5B	0.418227	0.587752	0.182885	0.033*
C6	0.613 (8)	0.709 (2)	0.253 (5)	0.025 (8)*
H6A	0.517313	0.762502	0.233300	0.037*
H6B	0.738025	0.727722	0.361484	0.037*
H6C	0.628155	0.702831	0.140546	0.037*
C7	0.703 (5)	0.494 (3)	0.153 (5)	0.017 (8)*
H7A	0.780548	0.430017	0.174116	0.021*
H7B	0.777263	0.552620	0.140771	0.021*
C8	0.516 (4)	0.482 (3)	−0.033 (5)	0.021 (9)*
H8A	0.546821	0.470602	−0.134755	0.032*
H8B	0.442106	0.423120	−0.025216	0.032*
H8C	0.438810	0.546083	−0.058658	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re	0.0322 (12)	0.0080 (4)	0.0215 (7)	0.0046 (17)	0.0207 (11)	0.004 (2)
S1	0.027 (8)	0.008 (3)	0.025 (8)	−0.001 (3)	0.005 (4)	0.005 (4)
S2	0.015 (7)	0.021 (4)	0.030 (6)	−0.003 (5)	0.010 (5)	−0.004 (4)
S3	0.025 (8)	0.027 (5)	0.039 (9)	0.006 (4)	0.025 (8)	0.006 (5)
S4	0.019 (6)	0.016 (5)	0.048 (9)	0.012 (5)	0.011 (6)	0.002 (7)

Geometric parameters (Å, º)

Re—S3	2.111 (9)	C3—H3B	0.9900
Re—S2	2.113 (10)	C4—H4A	0.9800
Re—S4	2.132 (10)	C4—H4B	0.9800
Re—S1	2.133 (7)	C4—H4C	0.9800
N—C5	1.51 (2)	C5—C6	1.53 (3)
N—C1	1.51 (2)	C5—H5A	0.9900
N—C3	1.52 (2)	C5—H5B	0.9900
N—C7	1.52 (2)	C6—H6A	0.9800
C1—C2	1.54 (3)	C6—H6B	0.9800
C1—H1A	0.9900	C6—H6C	0.9800
C1—H1B	0.9900	C7—C8	1.52 (3)

C2—H2A	0.9800	C7—H7A	0.9900
C2—H2B	0.9800	C7—H7B	0.9900
C2—H2C	0.9800	C8—H8A	0.9800
C3—C4	1.53 (3)	C8—H8B	0.9800
C3—H3A	0.9900	C8—H8C	0.9800
S3—Re—S2	110.3 (6)	C3—C4—H4A	109.5
S3—Re—S4	110.6 (6)	C3—C4—H4B	109.5
S2—Re—S4	108.0 (6)	H4A—C4—H4B	109.5
S3—Re—S1	109.8 (5)	C3—C4—H4C	109.5
S2—Re—S1	110.0 (4)	H4A—C4—H4C	109.5
S4—Re—S1	108.0 (5)	H4B—C4—H4C	109.5
C5—N—C1	109.4 (17)	N—C5—C6	116 (3)
C5—N—C3	109.9 (18)	N—C5—H5A	108.3
C1—N—C3	109.7 (18)	C6—C5—H5A	108.3
C5—N—C7	109.9 (18)	N—C5—H5B	108.3
C1—N—C7	109.5 (17)	C6—C5—H5B	108.3
C3—N—C7	108.5 (17)	H5A—C5—H5B	107.4
N—C1—C2	116 (2)	C5—C6—H6A	109.5
N—C1—H1A	108.2	C5—C6—H6B	109.5
C2—C1—H1A	108.2	H6A—C6—H6B	109.5
N—C1—H1B	108.2	C5—C6—H6C	109.5
C2—C1—H1B	108.2	H6A—C6—H6C	109.5
H1A—C1—H1B	107.3	H6B—C6—H6C	109.5
C1—C2—H2A	109.5	N—C7—C8	116 (2)
C1—C2—H2B	109.5	N—C7—H7A	108.3
H2A—C2—H2B	109.5	C8—C7—H7A	108.3
C1—C2—H2C	109.5	N—C7—H7B	108.3
H2A—C2—H2C	109.5	C8—C7—H7B	108.3
H2B—C2—H2C	109.5	H7A—C7—H7B	107.4
N—C3—C4	116 (3)	C7—C8—H8A	109.5
N—C3—H3A	108.3	C7—C8—H8B	109.5
C4—C3—H3A	108.3	H8A—C8—H8B	109.5
N—C3—H3B	108.3	C7—C8—H8C	109.5
C4—C3—H3B	108.3	H8A—C8—H8C	109.5
H3A—C3—H3B	107.4	H8B—C8—H8C	109.5