

Two polymorphs of tetraethyl-ammonium [hydrogen tris(3,5-dimethylpyrazolyl)borato]di- μ_2 -sulfido-disulfido(η^2 -tetrasulfido)-ditungsten(V) with $Z' = 1$ and 2

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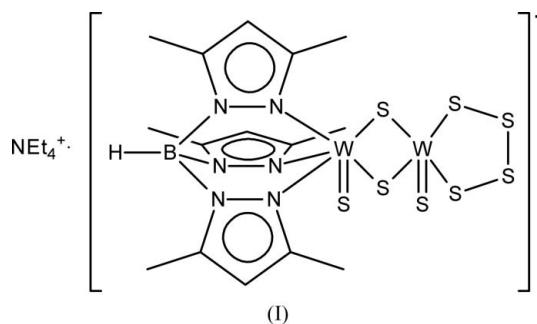
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Two polymorphs of the title compound, $(C_8H_{20}N)[W_2S_4(S_4)-(C_{15}H_{22}BN_6)]$, have been obtained unexpectedly by attempted recrystallization of a mixed-metal–sulfur cluster complex from different solvents. The dinuclear complex anion contains W^V in two different coordination environments, one of them distorted octahedral with a tris(pyrazolyl)borate anion, a terminal sulfide and two bridging sulfide ligands, the other distorted square-pyramidal with a terminal sulfide, two bridging sulfide and a chelating tetrasulfide ligand. The three independent anions in the two polymorphs have essentially the same geometry. The central W_2S_2 ring is a slightly folded rhombus with acute angles at the S atoms, and the WS_4 chelate ring is an envelope with one noncoordinating S atom as the flap. The second polymorph, with $Z' = 2$ and pseudo-inversion symmetry relating the anions of the asymmetric unit, also displays pseudo-translation features in its layer structure, and all examined crystals were found to be twinned, possibly as a consequence of this structural feature.

Comment

In a long-term research project investigating mixed-metal cluster compounds with thiometallate cores (see, for example, Beheshti *et al.*, 2007, 2008, 2011), we treated $(Et_4N)[Tp^*WS_3]$ [Tp^* is hydrogen tris(3,5-dimethylpyrazolyl)borate, an established tripodal ligand] with AgI in acetonitrile solution. Elemental analysis and electronic and vibrational spectroscopy of the crude product indicated a successful synthesis of the intended product $(Et_4N)[Tp^*WS_3(AgI)]$ in a type of reaction we have used many times previously; however, attempted recrystallization from acetonitrile solution by vapour diffusion of diethyl ether led to decomposition and the

unexpected isolation of the title complex, $(Et_4N)[Tp^*W_2S_2-(\mu_2-S)_2(S_4)]$, (I), which was identified by crystal structure determination. A second polymorph of the same complex was obtained when recrystallization of the initial crude product was attempted from acetone solution. We report here the structures of both polymorphs, one of which, (I-1), has $Z' = 1$ and the other, (I-2), has $Z' = 2$ and pseudo-inversion symmetry relating the two anions in the asymmetric unit.



The asymmetric unit of polymorph (I-1), containing one cation and one anion, is shown in Fig. 1. Figs. 2 and 3 show the two cations and two anions in the asymmetric unit of polymorph (I-2), the complete asymmetric unit being too complex and congested for a single figure. Selected bond lengths and angles are presented in the tables. The structure of polymorph (I-2), as is often the case with structures having $Z' > 1$, is less precisely determined than that of polymorph (I-1), and *PLATON* (Spek, 2009) suggests several possible twin laws, though none of these applied individually leads to an

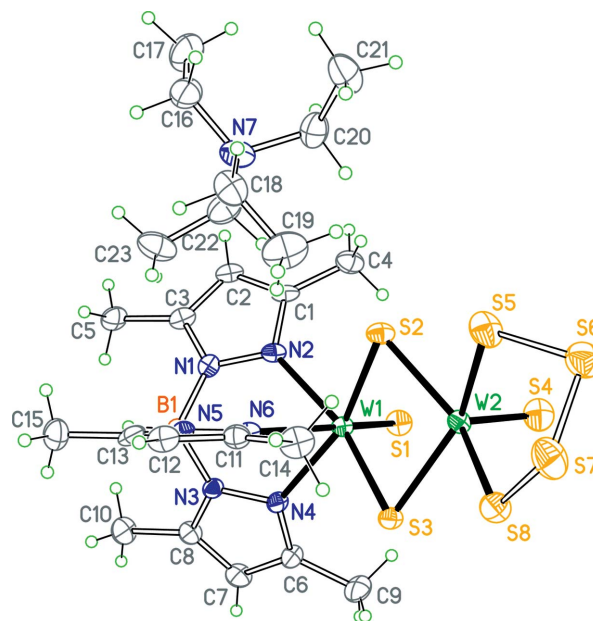


Figure 1

The asymmetric unit of polymorph (I-1), showing atom labels and displacement ellipsoids drawn at the 40% probability level for non-H atoms.

improvement in the refinement. Discussion of the geometry is based, therefore, mainly on the more precise structure of polymorph (I-1).

Comparison of the two anions in polymorph (I-2) with each other, and with the single anion in polymorph (I-1), using the molecule overlay feature of *Mercury* (Macrae *et al.*, 2008), shows that they are essentially identical, allowing for the chiral conformation of the WS_4 chelate ring, both enantiomers of which are present in each case in these centrosymmetric crystal structures: the r.m.s. deviations for overlays of all non-H atoms of the anions are 0.116 Å for the two anions of polymorph (I-2) (one of them inverted), and 0.267 and 0.271 Å for the anion of polymorph (I-1) with each of the anions of polymorph (I-2); corresponding values when the overlay is restricted to the five atoms of the WS_4 ring are 0.087, 0.103 and 0.081 Å, respectively. The cations show no significant variations except in the flexible C—C—N—C torsion angles.

The anion contains two W atoms, which have the same +5 oxidation state but quite different ligand sets and coordination geometries. One (W1 or W3) is six-coordinate with a distorted octahedral geometry, being bonded to a tridentate Tp^{*-} ligand in a necessarily facial configuration, one terminal sulfide ligand and two bridging sulfide ligands. The bite angles N—W—N of the Tp^{*-} ligand are reduced below the ideal *cis*-octahedral value of 90° by the constraints of the ligand internal geometry, and the three S—W—S angles are all more than 10° greater than 90°. The strong *trans* influence of the

terminal sulfide ligand causes the opposite W—N bond to be markedly longer than the other two.

The second W atom (W2 or W4) is five-coordinate with a distorted square-based pyramidal geometry. The apical position is occupied by a terminal sulfide ligand, while two mutually *cis* positions of the square base are taken by the bridging sulfide ligands and the other two by the chelating tetrasulfide ligand.

There are three different types of ligand containing only S atoms, *viz.* terminal sulfide, bridging sulfide and chelating tetrasulfide. Each of these has a formal 2− charge. The two sulfide bridges both link the two W atoms, forming a central four-membered ring with essentially equal sides but markedly acute angles at the S atoms. The ring is slightly folded, with an r.m.s. deviation of 0.222 Å for the four atoms from their mean plane. The WS_4 chelate ring has an envelope conformation, with one S atom [S6 in polymorph (I-1)] more than 1.0 Å out of the mean plane of the other four atoms; the central S—S bond of this ligand is significantly shorter than the other two.

A search of the Cambridge Structural Database (CSD, Version 5.31; Allen, 2002) shows that all previously reported structures of ditungsten (and also dimolybdenum) complexes with two bridging sulfide ligands and a chelating tetrasulfide ligand [*i.e.* with an $M(\mu-S)_2M(S_4)$ structural unit] contain exclusively sulfide (and/or oxide), disulfide and tetrasulfide ligands in various combinations, the total number of such structures (including redeterminations) being 17 with the following CSD refcodes and references: BIZVUB (Draganjac *et al.*, 1982); COZSIT (Huang *et al.*, 1984); DOFZIH (Cohen & Stiefel, 1985); DOFZIH01 (Chakrabarty *et al.*, 1996);

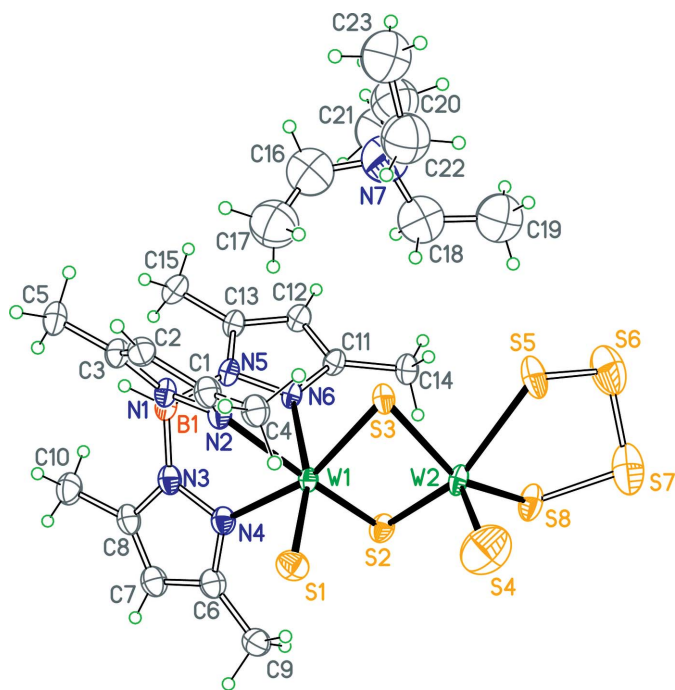


Figure 2

One cation and one anion of polymorph (I-2), showing atom labels and displacement ellipsoids drawn at the 40% probability level for non-H atoms.

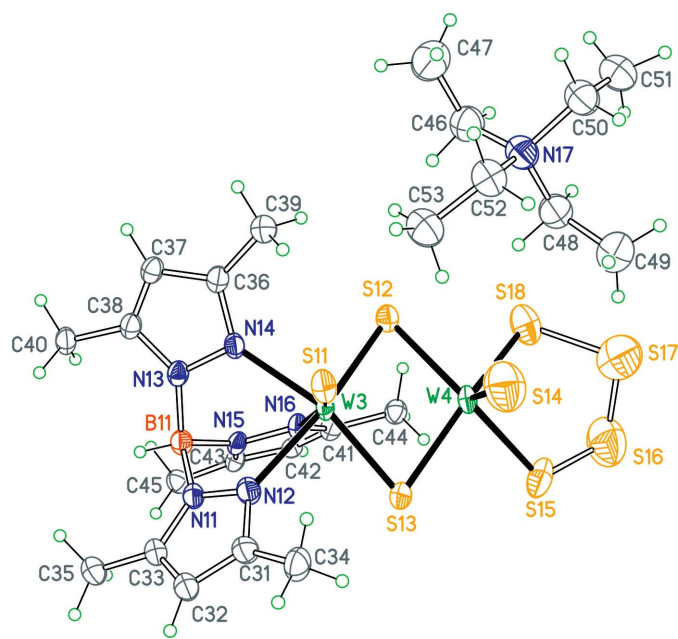


Figure 3

The other cation and anion of the asymmetric unit of polymorph (I-2), showing atom labels and displacement ellipsoids drawn at the 40% probability level for non-H atoms.

DOFZIH02 (Mukherjee *et al.*, 1997); DOYWAN, DOYWAP, DOYWET and DOYWIX (Müller *et al.*, 1985); FAGVIS (Coucounanis & Hadjikyriacou, 1986); FAGVIS10 (Hadjikyriacou & Coucounanis, 1987); KADFAW and KADFEA (Coucounanis & Koo, 1989); SULFMO (Clegg *et al.*, 1981); VAKGAP (Zhang *et al.*, 1987); VAKGAP01 (Bhattacharyya *et al.*, 1991); VOCMAB (Coucounanis *et al.*, 1991). These complexes, all of them anionic, thus contain only Mo/W, S and (in some cases) O atoms, and the title complex is unprecedented in this respect. There are six previous examples of complexes in which a tris(pyrazolyl)borate ligand is coordinated to an $M(\mu_2-S)_2M$ unit: FIBDAV (Young *et al.*, 1987); FIBDAV10 and GIJFUA (Roberts *et al.*, 1988); IMUPIP and IMUPOP (Seino *et al.*, 2003); QOZZOU (Eagle *et al.*, 1999). Only four reported structures contain both a tris(pyrazolyl)borate ligand and a tetrasulfide ligand bonded to metal atoms, two are indium complexes [NUXHUI (Kuchta & Parkin, 1996) and ZIPQAU (Reger & Coan, 1995)] and two are molybdenum complexes (QIXHOU and QIXHUA; Seino *et al.*, 2001); and in every case the two ligands are coordinated to a single metal centre. Individual features of the polymorphs of the title complex are similar to these various known structures, including comparable bond lengths in general, but the combination of the features is novel.

The two polymorphs differ primarily in their packing arrangements. While there is nothing remarkable about the packing in polymorph (I-1), the cations and anions in polymorph (I-2) are arranged in layers parallel to (001), as shown in Fig. 4. There are two layers in the unit-cell *c*-axis repeat.

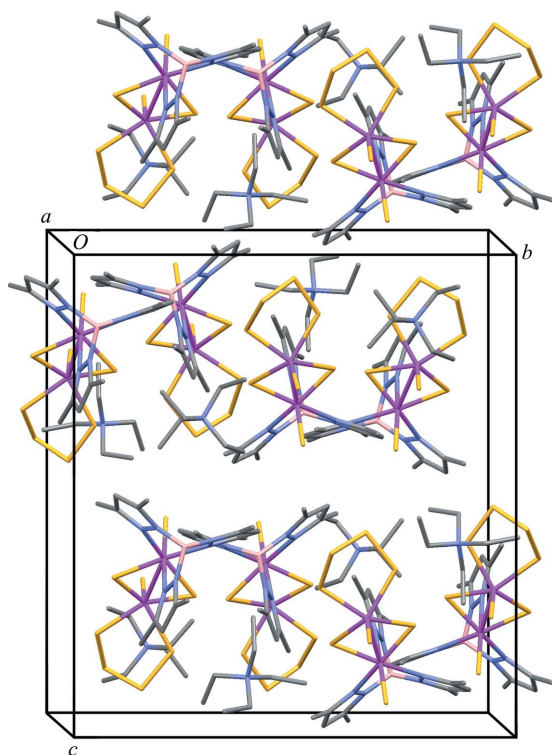


Figure 4

The packing of polymorph (I-2), viewed approximately along the *a* axis. H atoms have been omitted for clarity.

Each layer contains both independent cations and both independent anions. Anions in adjacent layers are related by pseudosymmetry; alternating translations of about 10.2 and 11.3 Å relate individual symmetry-inequivalent anions in a zigzag fashion, these pseudo-translation vectors being inclined at approximately 106 and 72° to the *b* axis. It is possible that stacking faults in the sequence of these layers may be responsible in interaction terms for the occurrence of twinning in this polymorph, such twinning being geometrically facilitated by the fact that β is close to 90°. They do not, however, lead to any significant diffuse streaks in the diffraction pattern.

The polymorphism and features of interest in the anion geometry and packing of these crystal structures are the unexpected outcome from an experiment originally designed to produce quite different chemical results.

Experimental

(Et₄N)[Tp*WS₃] (0.1 g, 0.14 mmol; Seino *et al.*, 2001) was dissolved in dry acetonitrile (20 ml) and AgI (0.1 g, 0.42 mmol) was added. After stirring for *ca* 1 h at room temperature, the mixture was centrifuged and the supernatant was evaporated to dryness under vacuum. The product separated as a brown powder together with AgI. The precipitate was then leached with CH₂Cl₂ (2 × 5 ml) to separate the soluble complex from AgI. The brown supernatant liquid was evaporated to dryness. The residue was washed with diethyl ether (2 × 3 ml) and dried *in vacuo* to give a brown powder (66.6 mg, 50% yield based on W). Similar reactions of (Et₄N)[Tp*WS₃] with AgI in a 1:4 molar ratio gave the same product. Analysis calculated: C 29.30, H 4.46, N 10.40%; found: C 29.60, H 4.50, N 10.51%; ¹H NMR (CDCl₃, 400 MHz): δ 1.38–1.41 (*t*, 12H, CH₃ in cation), 2.50 (*s*, 9H, CH₃ in Tp*), 3.08 (*s*, 9H, CH₃ in Tp*), 3.41–3.45 (*q*, 8H, CH₂ in cation), 6.18 (*s*, 3H, CH in Tp*), B–H was not located; IR spectrum (KBr disc): (W–S) 435 and 482 cm⁻¹, (B–H) 2554 cm⁻¹; UV–visible spectrum (MeCN, λ_{\max}): 240, 302, 376 nm.

This product decomposed during crystallization attempts by slow diffusion of diethyl ether into a saturated solution in acetonitrile or acetone at room temperature. Two crystal types suitable for X-ray structure determination were obtained and were subsequently found to be polymorphs; one was from MeCN/diethyl ether and the other from acetone/diethyl ether. On leaving a solution in MeCN to stand for 24 h, air-stable pale-yellow needle-shaped crystals of the known compound (Et₄N)₅[Ag₆I₁₁] (Zhao *et al.*, 1999) were obtained. After separation of these crystals by filtration, followed by slow diffusion of diethyl ether into the filtrate for 5 d at room temperature, deep-orange crystals of the title compound [polymorph (I-1)] were obtained. Analysis calculated: C 26.25, H 4.00, N 9.32%; found: C 27.73, H 4.52, N 9.69%; ¹H NMR (DMSO-*d*₆, 400 MHz): δ 1.15–1.19 (*m*, 12H, CH₃ of cation), 2.58 (*s*, 9H, CH₃ in Tp*), 2.84 (*s*, 9H, CH₃ in Tp*), 3.19–3.23 (*q*, 8H, CH₂ of cation), 5.29 (B–H), 6.36 (*s*, 3H, CH in Tp*); IR spectrum (KBr disc): W–S 434 and 490 cm⁻¹, S–S 515 cm⁻¹, B–H 2561 cm⁻¹; UV–visible spectrum (MeCN, λ_{\max}): 209, 242, 303 nm. Crystals of the second polymorph (giving essentially the same spectroscopic data) were obtained after two weeks by diffusion of diethyl ether into an acetone solution of the crude first product, no other compound being formed in this case.

The products of the two recrystallizations were not extensively examined to determine whether each was actually a pure single polymorph or whether a mixture was obtained in one or both cases, although several crystals from the acetone recrystallization were

examined in an attempt to measure better data and the second polymorph was identified in every case.

Polymorph (I-1)

Crystal data

(C₈H₂₀N)[W₂S₄(S₄)(C₁₅H₂₂BN₆)]
M_r = 1051.63
 Monoclinic, *P*2₁/*n*
a = 10.5173 (2) Å
b = 17.5635 (3) Å
c = 19.4889 (4) Å
 β = 104.878 (2)°

V = 3479.31 (11) Å³
Z = 4
 Mo *K*α radiation
 μ = 7.12 mm⁻¹
T = 150 K
 0.32 × 0.24 × 0.08 mm

Data collection

Oxford Diffraction Gemini A Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.210, *T_{max}* = 0.600

17702 measured reflections
 7333 independent reflections
 5814 reflections with *I* > 2σ(*I*)
R_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.098$
S = 1.09
 7333 reflections
 383 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 2.98 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.86 \text{ e \AA}^{-3}$

Polymorph (I-2)

Crystal data

(C₈H₂₀N)[W₂S₄(S₄)(C₁₅H₂₂BN₆)]
M_r = 1051.63
 Monoclinic, *P*2₁/*n*
a = 17.8602 (10) Å
b = 18.8742 (10) Å
c = 20.6188 (10) Å
 β = 90.343 (5)°

V = 6950.4 (6) Å³
Z = 8
 Mo *K*α radiation
 μ = 7.12 mm⁻¹
T = 150 K
 0.52 × 0.38 × 0.04 mm

Table 1

Selected geometric parameters (Å, °) for polymorph (I-1).

W1–S1	2.1348 (18)	W2–S3	2.3374 (16)
W1–S2	2.3224 (16)	W2–S4	2.091 (2)
W1–S3	2.3269 (17)	W2–S5	2.421 (2)
W1–N2	2.232 (5)	W2–S8	2.3960 (19)
W1–N4	2.235 (5)	S5–S6	2.019 (3)
W1–N6	2.343 (5)	S6–S7	1.994 (4)
W2–S2	2.3190 (18)	S7–S8	2.069 (3)
S1–W1–S2	104.94 (7)	S2–W2–S4	108.08 (8)
S1–W1–S3	104.05 (7)	S2–W2–S5	75.55 (7)
S1–W1–N2	89.53 (15)	S2–W2–S8	141.82 (7)
S1–W1–N4	89.77 (15)	S3–W2–S4	109.19 (7)
S1–W1–N6	162.42 (14)	S3–W2–S5	144.77 (7)
S2–W1–S3	100.29 (6)	S3–W2–S8	78.04 (6)
S2–W1–N2	83.74 (13)	S4–W2–S5	105.28 (8)
S2–W1–N4	161.83 (15)	S4–W2–S8	108.43 (8)
S2–W1–N6	86.39 (13)	S5–W2–S8	84.47 (8)
S3–W1–N2	164.13 (15)	W1–S2–W2	75.75 (5)
S3–W1–N4	86.05 (14)	W1–S3–W2	75.31 (5)
S3–W1–N6	86.69 (13)	W2–S5–S6	106.08 (12)
N2–W1–N4	85.82 (19)	S5–S6–S7	98.36 (14)
N2–W1–N6	78.20 (19)	S6–S7–S8	103.51 (14)
N4–W1–N6	76.93 (19)	W2–S8–S7	112.75 (12)
S2–W2–S3	100.08 (6)		

Data collection

Oxford Diffraction Gemini A Ultra diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.120, *T_{max}* = 0.765

23985 measured reflections
 11129 independent reflections
 6168 reflections with *I* > 2σ(*I*)
R_{int} = 0.119

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.171$
S = 0.97
 11129 reflections
 759 parameters

760 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 3.82 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -2.26 \text{ e \AA}^{-3}$

H atoms were allocated in geometrically calculated positions and refined with a riding model (including free rotation about C–C bonds), and with *U_{iso}* values constrained to be 1.2 (1.5 for methyl groups) times the *U_{eq}* of the carrier atom; the single exception to this was the H atom attached to the B atom in polymorph (I-1), the position of which was refined freely. For the lower-precision poly-

Table 2

Selected geometric parameters (Å, °) for polymorph (I-2).

W1–S1	2.144 (5)	W3–N12	2.241 (14)
W1–S2	2.314 (5)	W3–N14	2.193 (13)
W1–S3	2.318 (4)	W3–N16	2.371 (15)
W1–N2	2.265 (14)	W4–S12	2.328 (5)
W1–N4	2.246 (13)	W4–S13	2.320 (5)
W1–N6	2.329 (14)	W4–S14	1.939 (8)
W2–S2	2.322 (4)	W4–S15	2.406 (6)
W2–S3	2.331 (5)	W4–S18	2.386 (7)
W2–S4	1.859 (9)	S5–S6	2.060 (9)
W2–S5	2.448 (6)	S6–S7	1.975 (13)
W2–S8	2.423 (5)	S7–S8	2.059 (8)
W3–S11	2.124 (5)	S15–S16	1.954 (12)
W3–S12	2.330 (5)	S16–S17	1.857 (16)
W3–S13	2.316 (5)	S17–S18	2.018 (12)
S1–W1–S2	102.3 (2)	S12–W3–N12	165.7 (4)
S1–W1–S3	104.20 (18)	S12–W3–N14	87.4 (4)
S1–W1–N2	91.8 (4)	S12–W3–N16	85.9 (4)
S1–W1–N4	90.7 (4)	S13–W3–N12	84.0 (4)
S1–W1–N6	164.1 (3)	S13–W3–N14	158.4 (4)
S2–W1–S3	101.34 (16)	S13–W3–N16	85.6 (4)
S2–W1–N2	163.2 (4)	N12–W3–N14	83.5 (5)
S2–W1–N4	86.6 (4)	N12–W3–N16	81.1 (5)
S2–W1–N6	86.2 (4)	N14–W3–N16	75.1 (5)
S3–W1–N2	83.6 (4)	S12–W4–S13	100.92 (16)
S3–W1–N4	161.0 (4)	S12–W4–S14	109.0 (3)
S3–W1–N6	86.9 (4)	S12–W4–S15	143.2 (2)
N2–W1–N4	84.1 (5)	S12–W4–S18	77.7 (2)
N2–W1–N6	78.0 (5)	S13–W4–S14	105.6 (3)
N4–W1–N6	76.3 (5)	S13–W4–S15	80.3 (2)
S2–W2–S3	100.71 (15)	S13–W4–S18	147.1 (2)
S2–W2–S4	107.6 (4)	S14–W4–S15	105.9 (3)
S2–W2–S5	144.1 (2)	S14–W4–S18	105.8 (3)
S2–W2–S8	79.03 (17)	S15–W4–S18	82.0 (3)
S3–W2–S4	107.7 (3)	W1–S2–W2	76.14 (14)
S3–W2–S5	76.11 (17)	W1–S3–W2	75.90 (14)
S3–W2–S8	148.3 (2)	W2–S5–S6	112.2 (4)
S4–W2–S5	107.4 (4)	S5–S6–S7	100.9 (5)
S4–W2–S8	102.4 (3)	S6–S7–S8	100.0 (4)
S5–W2–S8	85.8 (2)	W2–S8–S7	106.7 (3)
S11–W3–S12	101.65 (19)	W3–S12–W4	75.31 (15)
S11–W3–S13	104.80 (19)	W3–S13–W4	75.71 (16)
S11–W3–N12	89.8 (4)	W4–S15–S16	117.4 (5)
S11–W3–N14	92.7 (4)	S15–S16–S17	98.5 (6)
S11–W3–N16	165.5 (3)	S16–S17–S18	103.5 (7)
S12–W3–S13	100.99 (16)	W4–S18–S17	104.1 (4)

morph (I-2), which may be subject to unresolved multiple twinning, restraints (similarity and rigid-bond) were applied to all displacement parameters, and bond-length and angle similarity restraints were applied to the tetraethylammonium cations. Several crystals of this polymorph were examined and two complete data sets were measured from different crystals. In each case, the crystals were not single, with at least two components for which the same unit cell could be found in different orientations. Following a number of attempted approaches, the best result was obtained by extracting integrated intensity data for two dominant components of one crystal and then using one of these components and rejecting reflections that were overlapped with the second component. Significantly poorer refinement resulted from full multi-component data sets and other similar treatments of overlap of the component diffraction patterns.

More reflections than usual were rejected in the data integration and processing stages for polymorph (I-2) because of poor profile fitting and related problems; these are probably caused by twinning effects, which are suggested on the basis of unit-cell parameters and comparisons of observed and calculated structure factors by *PLATON* (Spek, 2009), and are likely to involve split reflection profiles.

For both polymorphs, data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BI3009). Services for accessing these data are described at the back of the journal.

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