Synthesis and absolute structure of (R)-2-(benzylselanyl)-1-phenylethanaminium hydrogen sulfate monohydrate: crystal structure and Hirshfeld surface analyses

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A hydrogen sulfate salt, C15H18NSe+C1HSO4+C0H2O or [BnSeCH2CH(Ph)NH3+] (HSO4−), of a chiral selenated amine (R)-2-(benzylselanyl)-1-phenylethanamine (BnSeCH2CH(Ph)NH2) has been synthesized and characterized by elemental analysis,1H and 13C{1H} NMR, FT–IR analysis, and single-crystal X-ray diffraction studies. The title salt crystallizes in the monohydrate form in the non-centrosymmetric monoclinic P21 space group. The cation is somewhat W shaped with the dihedral angle between the two aromatic rings being 60.9 (4)°. The carbon atom attached to the amine nitrogen atom is chiral and in the R configuration, and, the –C—C– bond of the –CH2—CH– fragment has a staggered conformation. In the crystal structure, two HSO4− anions and two water molecules form an R44(12) tetrameric type of assembly comprised of alternating HSO4− anions and water molecules via discrete D(2) O–H···O hydrogen bonds. This tetrameric assembly aggregates along the b-axis direction as an infinite one-dimensional tape. Adjacent tapes are interconnected via discrete D(2) N–H···O hydrogen bonds between the three amino hydrogen atoms of the cation sandwiched between the two tapes and the three HSO4− anions of the nearest asymmetric units, resulting in a complex two-dimensional sheet along the ab plane. The pendant arrangement of the cations is stabilized by C−H···π interactions between adjacent cations running as chains down the [010] axis. Secondary Se···O [3.1474 (4) Å] interactions are also observed in the crystal structure. A Hirshfeld surface analysis, including dnorm, shape-index and fingerprint plots of the cation, anion and solvent molecule, was carried out to confirm the presence of various interactions in the crystal structure.

1. Chemical context

Selenium is an important bio-element (Schwarz et al., 1957; Papp et al., 2007). The hypervalent nature of selenium results in interesting secondary bonding interactions (SBIs), also known as non-bonded interactions, in organoselenium compounds (Musher et al., 1969; Raghavendra Kumar et al., 2006; Chivers & Laitinen, 2015; Bleiholder et al., 2006). These structural aspects are worth exploring as weak SBIs (Iwaoka et al., 2001, 2002a,b) in the compounds of heavy chalcogens (Se and Te) are ascribed important roles in structural chemistry, such as the stabilization of otherwise unstable organo-chalcogen compounds and supramolecular associations (Tiekink & Zukerman-Schpector, 2010; Werz et al., 2002) and possessing biological activities (Reich et al., 2016; Bartolini et al., 2017; Engman et al., 1992; Mukherjee et al., 2010). Some
organoselenated alkyl/arylamines have been synthesized (Singh & Srivastava, 1990; Srivastava et al., 1994; Revanna et al., 2015), but further investigations on their single-crystal X-ray structures, especially of chiral derivatives, are limited (Musher et al., 1969; Raghavendra Kumar et al., 2006; Chivers & Laitinen, 2015; Bleiholder et al., 2006, Prabhu Kumar et al., 2019). Therefore, the synthesis and discussions on the single-crystal structural features of (R)-2-(benzylselanyl)-1-phenylethanaminium hydrogen sulfate monohydrate, [BnSeCH2CH(Ph)NH3]+(HSO4−), are the subject of the present paper.

2. Structural commentary

The title salt (Fig. 1) is formed by the transfer of a proton from sulfuric acid to the chiral selenated amine C15H18SeN. The asymmetric unit of the structure consists of one (C15H18SeN)+ cation, one HSO4− anion and a solvent water molecule with no direct hydrogen-bonding interactions between them. In the HSO4− ion, three of the S—O bond lengths are almost the same, falling in the range of 1.447 (4)–1.452 (5) Å, while the fourth is slightly elongated at 1.527 (5) Å. This suggests that the three nearly identical S—O bonds have partial double-bond character owing to resonance, while the fourth S—O bond has single-bond character. This validates the formation of the salt via single proton transfer from sulfuric acid to the amine. The title salt crystallizes in the monoclinic form in the monohydrate form in the present paper.

The carbon atom attached to the amine nitrogen atom is a chiral atom with an R configuration and the –C—C— bond of the –CH2—CH– fragment has a staggered conformation.

Figure 1
A view of the molecular structure of the title salt, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

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

| D—H—A | D—H | H—A | D—A | D—H—A |
|--------|-----|-----|-----|-------|
| N1—H1A···O4iv | 0.89 | 2.16 | 3.003 (7) | 157 |
| N1—H1B···O4vi | 0.89 | 2.05 | 2.893 (6) | 159 |
| N1—H1C···O2vi | 0.89 | 1.92 | 2.812 (6) | 176 |
| O1—H1D···O2vi | 0.85 | 1.91 | 2.726 (8) | 161 |
| O1—H1E···O5v | 0.85 | 1.95 | 2.730 (6) | 152 |
| O3—H3A···O1 | 0.82 | 1.68 | 2.483 (9) | 167 |
| C15—H15···Cgvi | 0.93 | 2.75 | 3.547 (7) | 144 |

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

3. Supramolecular features

The crystal structure features, by virtue of its salt form, several strong-to-moderate hydrogen bonds, which are not seen to the same extent in the reported freebase structure of the closely related compound (S)-1-(benzylselanyl)-3-phenylpropan-2-amine (Prabhu Kumar et al., 2019). The general rule that all strong hydrogen-bond donors participate in hydrogen bonding with strong hydrogen-bond acceptors is totally satisfied in this salt, with all the strong donors and acceptors in the cation, anion and the solvent being involved in at least one hydrogen bond. In the crystal structure, two HSO4− anions and two water molecules are interconnected to form a tetrameric type of assembly comprising of alternating HSO4− anions and water molecules via discrete D(2) O1—H1D···O2, O1—H1E···O5 and O3—H3A···O1 hydrogen bonds (Fig. 2, Table 1), with the O1—H1E···O5 hydrogen bond appearing twice. This tetrameric type of assembly having a R21(12) graph-set notation aggregates along the b-axis direction as an infinite one dimensional tape, with adjacent tetrameric units in the tape glued to each other through the common O1—H1E···O5 hydrogen bonds (Fig. 2). The O1—H1D···O2 and O1—H1E···O5 hydrogen bonds have structure-directing features along the [010] axis. Adjacent tapes, which are 5.2133 (4) Å...
4. Hirshfeld surface analyses

The Hirshfeld surfaces including $d_{norm}$ and shape-index and fingerprint (FP) analyses of the cation, anion and the solvent are shown in Figs. 4 and 5. In the $d_{norm}$ surface of the cation (highlighting O···H/H···O contacts only; Fig. 4a), dark-red spots in the proximity of three amino hydrogen atoms are a result of strong N1···H1A···O4, N1···H1B···O4 and N1···H1C···O2 hydrogen bonds between the cation and HSO$_4^-$ anions. Further, the Hirshfeld surface of the cation mapped over shape-index (highlighting C···H/H···C contacts only; Fig. 4b) shows a dark-red spot close to the centroid of the C1–C6 ring facing the H15 hydrogen atom, which is due to the C15–H15···π ($\pi$ electrons of the C1–C6 ring) interactions observed between adjacent cations. The overall FP plot and those decomposed to individual atom···atom contacts contributing to the Hirshfeld surfaces of the cation are shown in Fig. 4c, 4d, 4e and 4f, respectively. The highest contribution to the Hirshfeld surface is from H···H dispersions, which contribute 48.4%, followed by C···H/H···C (26%), O···H/H···O (17.8%), Se···H/H···Se (5.7%) and others (2.1%). The symmetry about the $d_i = d_e$ axis passing through the origin observed in the FP plots for the H···H and C···H/H···C contacts suggests that these interactions exist only between the cationic species and not between cation–anion or cation–water. The asymmetric nature of the FP of the O···H/H···O contacts about the $d_i = d_e$ axis suggests that the O···H interactions are between unlike species, which is in agreement with the observed N···H···O interactions between cations and anions. A single spike observed in the FP of O···H/H···O contacts is characteristic of a strong or a moderate hydrogen bond. The spike observed at $d_i + d_e \sim 1.9$ Å is very close to the H1C···O2 distance of 1.92 Å (Table 1), thus supporting the participation of the cations in various N···H···O hydrogen bonds. Two blunt spikes (a characteristic of a weak interaction between like species) observed in the FP of C···H/H···C contacts at $d_i + d_e \sim 2.8$ Å is very close to the H15···Cg distance of 2.75 Å (Table 1), thereby confirming the presence

4. Hirshfeld surface analyses

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of C—H⋯π interactions between the cations. Thus, the Hirshfeld surface analysis provides adequate and reliable evidence, both qualitatively (in terms of pictorial depiction) and quantitatively, for the various interactions in which the cations participate. Analysis of the Hirshfeld surfaces of the anion and the solvent molecule gives similar results (Fig. 5). In the case of the anion, the highest contribution to the Hirshfeld surface is from O⋯H/H⋯O contacts, contributing 88.6%, while for the Hirshfeld surface of water, 61.6% is from O⋯H/H⋯O contacts and the remaining 38.4% is from H⋯H dispersions.

5. Database survey

The cation of the reported structure is somewhat similar to that observed in a closely related structure, (S)-1-(benzylselanyl)-3-phenylpropan-2-amine (Prabhu Kumar et al., 2019), which is homologous to the cation of the title salt with one additional —CH₂— group between the chiral carbon atom and its nearest aromatic ring. The configurations of the chiral carbon atom are different in the two structures. The dihedral angle between the aromatic rings in the related molecule is 66.49 (12°), which is very similar to that observed in the title structure. No intramolecular N—H⋯Se interaction is observed in the molecular cation of the present structure, unlike in the related molecule where one is observed. In the crystal of the related amine, the molecules are linked by weak N—H⋯N interactions, generating chains along the [100] direction.

6. Synthesis and crystallization

6.1. Materials and methods

Chemical reagents were purchased from Sigma–Aldrich (India) and used without further purification unless stated otherwise. For chemical synthesis, reactions were carried out in distilled water or in laboratory-grade solvents at room temperature. Melting points were determined in capillary tubes closed at one end and were reported uncorrected. IR spectra were recorded on a Jasco FT–IR-4100 spectrometer. Specific optical rotations (SOR) were measured on a Rudolph Autopol-I automatic polarimeter using a cell of 100 mm path length. ¹H and ¹³C [¹H] NMR spectra were recorded on an AVANCE-II Bruker 400 MHz spectrometer. (R)-1-(Benzylselanyl)-2-phenylethan-2-amine was synthesized according to our reported literature procedure (Revanna et al., 2015).

6.2. Synthesis of (1R)-2-(benzylselanyl)-1-phenthylan-1-ammoniumhydrogensulfate

The chiral selenated amine (R)-2-(benzylselanyl)-1-phenylethanamine was synthesized by a sequence of reactions shown in the reaction scheme starting from (2R)-2-amino-2-phenylethan-1-ol [derived from amino acid (R)-phenylglycinal] as per the literature procedure (Revanna et al., 2015). The title salt of the above amine was obtained by treating it with sulfuric acid (5 M) in methanol under ice-cold conditions.

To an ice-cold methanolic (5 mL) solution of (2R)-1-(benzylselanyl)-2-phenylethan-2-amine (0.291 g, 1 mmol) was added 5 M of H₂SO₄ (2 mL) under stirring. The resulting precipitate was stirred for a further hour at the same temperature. Then the precipitate was filtered and washed twice with cold methanol (10 mL × 2). The white solid obtained was recrystallized from hot methanol (10 mL), which afforded colourless crystals of the title salt. The salt is soluble in water, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), but insoluble in methanol, chloroform, dichloromethane, ether, tetrahydrofuran (THF) and hydrocarbon solvents such as n-hexane, benzene and toluene.

Yield: 92%; m.p. 469–472 K; (c 1.0 in MeOH). Elemental analysis: found C, 46.51; H, 4.88; N, 3.54. Calculated for C₁₅H₁₉N₇Se·HSO₄·H₂O: C, 46.39; H, 4.93; N, 3.61%. FT–IR (KBr, ν cm⁻¹): 3452, 3027, 2924, 1611, 1537, 1186, 693, 556, 477; ¹H NMR (DMSO-d₆, 400.233 MHz, δ ppm): 2.867–3.060 (dd, 2H, J = 9.2, 6.0 Hz, CH₂Se), 3.645 (s, 2H, SeCH₂), 4.329–4.351 (m, 1H, CH), 7.166–7.288 (m, 5H, ArH), 7.373–7.440 (m, 5H, ArH), 8.54 (bs, 3H, NH₃⁺), 1C¹H (δ ppm): 26.99 (CH₂Se), 27.15 (SeCH₂), 54.75

Table 2

| Experimental details. |
|-----------------------|
| Crystal data          |
| Chemical formula      | C₁₅H₁₉N₇Se·HSO₄·H₂O |
| M₀                    | 406.35              |
| Crystal system, space group | Monoclinic, P2₁ |
| Temperature (K)       | 293                 |
| a, b, c (Å)          | 10.4266 (4), 6.0539 (2), 14.2168 (7) |
| V (Å³)               | 897.38 (6)          |
| Z                    | 2                   |
| Radiation type       | Mo Kα               |
| μ (mm⁻¹)             | 2.23                |
| Crystal size (mm)    | 0.22 × 0.18 × 0.16  |

Data collection

| Diffraclometer        | Bruker APEXI II CCD area |
| Absorption correction | Multi-scan (SADABS; Bruker, 2009) |
| Tmin, Tmax            | 0.624, 0.700 |
| No. of measured reflections & observed [I > 2σ(I)] reflections | 4255, 3088, 2624 |
| Rmin (sin θ/λ)max (Å⁻¹) | 0.035 |
| Rmin (sin θ/λ)max (Å⁻¹) | 0.649 |

Refinement

| R[F² > 2σ(F²)], wR(F²), S | 0.044, 0.113, 0.99 |
| No. of reflections | 3088 |
| No. of parameters | 213 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 0.40, −0.48 |
| Absolute structure | Flack x determined using 665 quotients [(T(I)–(T)][(T(I)+(T))⁻¹] (Parsons et al., 2013) | 0.002 (16) |

Absolute structure parameter

Computer programs: APEXI2, SAINT-Plus and XPREP (Bruker, 2009), SHELXT2016/4 (Sheldrick, 2015a), SHELXL2016/4 (Sheldrick, 2015b) and Mercury (Macrae et al., 2020).

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7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were positioned with idealized geometry and refined using a riding model: C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms, C–H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene H atoms and C–H = 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methine H atoms. The amino H atoms and O-bound H atoms were also positioned geometrically and refined as riding: N–H = 0.89 Å with $U_{iso}(H) = 1.2U_{eq}(N)$; O$_{water}$–H = 0.85 Å with $U_{iso}(H) = 1.5U_{eq}(O_{water})$; O$_{anion}$–H = 0.82 Å with $U_{iso}(H) = 1.5U_{eq}(O_{anion})$.

Funding information

PRK thanks the Department of Science and Technology–SERB, New Delhi, India, for financial support in the form of project No. DST/SR/S1/IC-76/2010(G).

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Computing details

Data collection: \textit{APEX2} (Bruker, 2009); cell refinement: \textit{APEX2} and \textit{SAINT-Plus} (Bruker, 2009); data reduction: \textit{SAINT-Plus} and \textit{XPREP} (Bruker, 2009); program(s) used to solve structure: \textit{SHELXT2016/4} (Sheldrick, 2015a); program(s) used to refine structure: \textit{SHELXL2016/4} (Sheldrick, 2015b); molecular graphics: \textit{Mercury} (Macrae \textit{et al.}, 2020); software used to prepare material for publication: \textit{SHELXL2016/4} (Sheldrick, 2015b).

\[(R)-2-\text{(benzylselanyl)}-1\text{-phenylethanaminium hydrogen sulfate monohydrate}

\textbf{Crystal data}

\[
\text{C}_{15}\text{H}_{18}\text{NSe}^+\cdot\text{HSO}_4^-\cdot\text{H}_2\text{O}
\]

\[
M_r = 406.35
\]

Monoclinic, \(P2_1\)

Hall symbol: \(P2yb\)

\[
a = 10.4266 (4) \text{ Å}
\]

\[
b = 6.0539 (2) \text{ Å}
\]

\[
c = 14.2168 (7) \text{ Å}
\]

\[
\beta = 90.261 (4) ^\circ
\]

\[
V = 897.38 (6) \text{ Å}^3
\]

\[
Z = 2
\]

\[
F(000) = 416
\]

Prism

\[
D_{\text{x}} = 1.504 \text{ Mg m}^{-3}
\]

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 1021 reflections

\[
\theta = 2.4-27.5 ^\circ
\]

\[
\mu = 2.23 \text{ mm}^{-1}
\]

\[
T = 293 \text{ K}
\]

Prism, colourless

\[
0.22 \times 0.18 \times 0.16 \text{ mm}
\]

\textbf{Data collection}

Bruker APEXII CCD area diffractometer

4255 measured reflections

3088 independent reflections

2624 reflections with \(I > 2\sigma(I)\)

\[
R_{\text{int}} = 0.035
\]

\[
\theta_{\text{max}} = 27.5 ^\circ, \theta_{\text{min}} = 2.4 ^\circ
\]

\[
\begin{align*}
  h & = -12\rightarrow13 \\
  k & = -6\rightarrow7 \\
  l & = -16\rightarrow18
\end{align*}
\]

\textbf{Refinement}

Refinement on \(F^2\)

Least-squares matrix: full

\[
R[F^2 > 2\sigma(F^2)] = 0.044
\]

\[
wR(F^2) = 0.113
\]

\[
S = 0.99
\]

3088 reflections

213 parameters

\[
\begin{align*}
  \Delta\sigma/\sigma & < 0.001 \\
  \Delta\rho_{\text{max}} & = 0.40 \text{ e Å}^{-3}
\end{align*}
\]
Δρ_{\text{min}} = −0.48 \text{ e Å}^{-3}

Absolute structure: Flack x determined using 665 quotients [(I)−(I)]/[(I)+(I)] (Parsons et al., 2013)
Absolute structure parameter: 0.002 (16)

Special details

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

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

|    | x     | y     | z     | U_{iso}/U_{eq} |
|----|-------|-------|-------|----------------|
| O2 | 0.2505 (4) | −0.0248 (8) | −0.0946 (4) | 0.0611 (14) |
| C3 | −0.0762 (7) | −0.6548 (14) | −0.3497 (6) | 0.067 (2) |
| H3 | −0.038625 | −0.793146 | −0.342466 | 0.080* |
| C2 | −0.1040 (6) | −0.5295 (12) | −0.2720 (6) | 0.0556 (19) |
| H2 | −0.086191 | −0.584727 | −0.212284 | 0.067* |
| N1 | −0.5188 (4) | 0.2116 (9) | −0.1128 (3) | 0.0392 (13) |
| H1A | −0.531807 | 0.355694 | −0.104787 | 0.047* |
| H1B | −0.466298 | 0.161851 | −0.068113 | 0.047* |
| H1C | −0.593408 | 0.140600 | −0.109508 | 0.047* |
| O4 | 0.3706 (4) | −0.3492 (8) | −0.0578 (3) | 0.0476 (11) |
| O3 | 0.1539 (5) | −0.3689 (10) | −0.1198 (4) | 0.0627 (14) |
| H3A | 0.136250 | −0.489162 | −0.096649 | 0.094* |
| O1 | 0.0666 (5) | −0.7188 (11) | −0.0553 (7) | 0.097 (2) |
| H1D | 0.114172 | −0.832572 | −0.058680 | 0.145* |
| H1E | −0.007149 | −0.769210 | −0.041900 | 0.145* |
| SE1 | −0.35634 (5) | −0.25057 (7) | −0.14135 (4) | 0.04370 (19) |
| S1 | 0.24573 (11) | −0.2451 (4) | −0.05445 (9) | 0.0386 (3) |
| O5 | 0.1938 (3) | −0.2455 (14) | 0.0397 (3) | 0.0577 (11) |
| C6 | −0.1847 (6) | −0.239 (2) | −0.3707 (5) | 0.0576 (17) |
| H6 | −0.218500 | −0.097722 | −0.378626 | 0.069* |
| C10 | −0.5289 (5) | 0.3042 (9) | −0.2820 (4) | 0.0377 (16) |
| C15 | −0.4578 (6) | 0.3885 (12) | −0.3559 (5) | 0.0449 (15) |
| H15 | −0.370318 | 0.359532 | −0.359223 | 0.054* |
| C4 | −0.1034 (7) | −0.5772 (18) | −0.4374 (7) | 0.077 (3) |
| H4 | −0.084348 | −0.662521 | −0.489933 | 0.092* |
| C1 | −0.1588 (5) | −0.3192 (11) | −0.2815 (5) | 0.0463 (16) |
| C9 | −0.4594 (5) | 0.1722 (10) | −0.2082 (4) | 0.0360 (13) |
| H9 | −0.370076 | 0.222507 | −0.205826 | 0.043* |
| C12 | −0.7151 (7) | 0.4805 (15) | −0.3469 (6) | 0.068 (2) |
| H12 | −0.802097 | 0.513070 | −0.342967 | 0.081* |
| C14 | −0.5161 (7) | 0.5156 (13) | −0.4248 (5) | 0.0546 (18) |
| H14 | −0.467590 | 0.568783 | −0.474659 | 0.066* |
| C8 | −0.4598 (6) | −0.0755 (10) | −0.2284 (5) | 0.0404 (14) |
| H8A | −0.428439 | −0.099360 | −0.291714 | 0.048* |
| H8B | −0.547581 | −0.128372 | −0.226248 | 0.048* |
C11  $-0.6591 (6)$  0.3503 (14)  $-0.2794 (5)$  0.0573 (19)
H11  $-0.708984$  0.292124  $-0.231368$  0.069*
C13  $-0.6443 (7)$  0.5641 (14)  $-0.4206 (5)$  0.061 (2)
H13  $-0.682844$  0.651632  $-0.466410$  0.073*
C7  $-0.1873 (6)$  $-0.1864 (11)$  $-0.1955 (5)$  0.0531 (19)
H7A  $-0.183063$  $-0.030709$  $-0.211244$  0.064*
H7B  $-0.121754$  $-0.215704$  $-0.148436$  0.064*
C5  $-0.1593 (8)$  $-0.3717 (18)$  $-0.4485 (6)$  0.075 (3)
H5  $-0.180219$  $-0.321648$  $-0.508514$  0.090*

Atomic displacement parameters (Å²)

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O2 | 0.050 (3) | 0.044 (3) | 0.089 (4) | 0.003 (2) | 0.009 (3) | 0.018 (3) |
| C3 | 0.048 (4) | 0.058 (5) | 0.094 (7) | 0.000 (4) | 0.012 (4) | 0.013 (5) |
| C2 | 0.044 (4) | 0.048 (4) | 0.074 (5) | 0.005 (3) | $-0.001 (3)$ | 0.001 (4) |
| N1 | 0.050 (2) | 0.034 (4) | 0.033 (2) | 0.002 (2) | $-0.0048 (19)$ | $-0.002 (2)$ |
| O4 | 0.038 (2) | 0.052 (3) | 0.053 (3) | 0.012 (2) | 0.0011 (19) | 0.001 (2) |
| O3 | 0.057 (3) | 0.068 (3) | 0.064 (3) | $-0.017 (3)$ | $-0.014 (3)$ | 0.002 (3) |
| O1 | 0.050 (3) | 0.044 (4) | 0.197 (7) | 0.001 (3) | 0.022 (4) | 0.008 (4) |
| SE1 | 0.0484 (3) | 0.0345 (3) | 0.0482 (3) | 0.0023 (4) | 0.0009 (2) | $-0.0026 (4)$ |
| S1 | 0.0342 (6) | 0.0356 (6) | 0.0460 (7) | 0.0004 (10) | 0.0002 (5) | 0.0031 (11) |
| O5 | 0.048 (2) | 0.077 (3) | 0.049 (2) | 0.010 (3) | 0.0103 (18) | 0.004 (4) |
| C6 | 0.050 (3) | 0.060 (4) | 0.064 (4) | $-0.014 (5)$ | 0.011 (3) | 0.006 (6) |
| C10 | 0.038 (3) | 0.037 (4) | 0.038 (3) | $-0.002 (2)$ | 0.001 (2) | $-0.001 (2)$ |
| C15 | 0.045 (3) | 0.048 (4) | 0.041 (4) | $-0.002 (3)$ | 0.002 (3) | 0.002 (3) |
| C4 | 0.056 (5) | 0.089 (7) | 0.084 (7) | $-0.011 (5)$ | 0.028 (5) | $-0.032 (6)$ |
| C1 | 0.034 (3) | 0.042 (4) | 0.062 (4) | $-0.005 (3)$ | 0.007 (3) | $-0.002 (3)$ |
| C9 | 0.039 (3) | 0.032 (3) | 0.037 (3) | $-0.001 (2)$ | 0.002 (2) | $-0.001 (2)$ |
| C12 | 0.044 (4) | 0.093 (7) | 0.065 (5) | 0.006 (4) | $-0.014 (4)$ | 0.015 (5) |
| C14 | 0.072 (5) | 0.055 (4) | 0.037 (4) | $-0.005 (4)$ | 0.004 (3) | 0.009 (3) |
| C8 | 0.044 (3) | 0.036 (3) | 0.041 (3) | $-0.003 (3)$ | $-0.003 (3)$ | $-0.012 (3)$ |
| C11 | 0.039 (3) | 0.079 (5) | 0.054 (4) | 0.000 (3) | 0.003 (3) | 0.009 (4) |
| C13 | 0.065 (5) | 0.065 (5) | 0.053 (5) | 0.008 (4) | $-0.017 (4)$ | 0.010 (4) |
| C7 | 0.043 (3) | 0.051 (5) | 0.065 (4) | $-0.004 (3)$ | 0.000 (3) | $-0.011 (3)$ |
| C5 | 0.060 (5) | 0.103 (7) | 0.063 (5) | $-0.019 (5)$ | 0.012 (4) | 0.008 (5) |

Geometric parameters (Å, °)

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| O2—S1 | 1.452 (5) | C10—C11 | 1.386 (8) |
| C3—C4 | 1.361 (13) | C10—C9 | 1.503 (8) |
| C3—C2 | 1.373 (10) | C15—C14 | 1.384 (9) |
| C3—H3 | 0.9300 | C15—H15 | 0.9300 |
| C2—C1 | 1.402 (10) | C4—C5 | 1.383 (14) |
| C2—H2 | 0.9300 | C4—H4 | 0.9300 |
| N1—C9 | 1.512 (7) | C1—C7 | 1.495 (9) |
| N1—H1A | 0.8900 | C9—C8 | 1.527 (8) |
| N1—H1B | 0.8900 | C9—H9 | 0.9800 |
N1—H1C 0.8900 C12—C11 1.370 (10)
O4—S1 1.447 (4) C12—C13 1.380 (11)
O3—S1 1.527 (5) C12—H12 0.9300
O3—H3A 0.8200 C14—C13 1.370 (10)
O1—H1D 0.8500 C14—H14 0.9300
O1—H1E 0.8500 C8—H8A 0.9700
Se1—C8 1.951 (6) C8—H8B 0.9700
Se1—C7 1.965 (6) C11—H11 0.9300
S1—O5 1.447 (4) C13—H13 0.9300
C6—C1 1.384 (10) C7—H7A 0.9700
C6—C5 1.395 (13) C7—H7B 0.9700
C6—H6 0.9300 C5—H5 0.9300
C10—C15 1.387 (8)

C4—C3—C2 120.2 (8) C2—C1—C7 119.5 (7)
C4—C3—H3 119.9 C10—C9—N1 110.1 (4)
C2—C3—H3 119.9 C10—C9—C8 112.9 (5)
C3—C2—C1 120.8 (8) N1—C9—C8 108.8 (5)
C3—C2—H2 119.6 C10—C9—H9 108.3
C1—C2—H2 119.6 N1—C9—H9 108.3
C9—N1—H1A 109.5 C8—C9—H9 108.3
C9—N1—H1B 109.5 C8—C9—H9 108.3
H1A—N1—H1B 109.5

C9—N1—H1C 109.5 C13—C12—C11 112.9 (5)

H1A—N1—H1C 109.5 C13—C12—C11 112.9 (5)
H1B—N1—H1C 109.5 C13—C12—C11 112.9 (5)

S1—O3—H3A 104.5 C9—C8—Se1 114.4 (4)

C3—C4—C5 120.1 (9) C9—C8—H8A 108.7
C3—C4—H4 120.0 C9—C8—H8B 108.7
C5—C4—H4 120.0 C9—C8—H8B 108.7

C6—C5 1.395 (13) C9—C8—H8B 108.7
C6—H6 0.9300 C9—C8—H8B 108.7
C10—C15 1.387 (8)

N1—H1C 0.8900 C12—C11 1.370 (10)
O4—S1 1.447 (4) C12—C13 1.380 (11)
O3—S1 1.527 (5) C12—H12 0.9300
O3—H3A 0.8200 C14—C13 1.370 (10)
O1—H1D 0.8500 C14—H14 0.9300
O1—H1E 0.8500 C8—H8A 0.9700
Se1—C8 1.951 (6) C8—H8B 0.9700
Se1—C7 1.965 (6) C11—H11 0.9300
S1—O5 1.447 (4) C13—H13 0.9300
C6—C1 1.384 (10) C7—H7A 0.9700
C6—C5 1.395 (13) C7—H7B 0.9700
C6—H6 0.9300 C5—H5 0.9300
C10—C15 1.387 (8)
C6—C1—C7 121.5 (7)

C4—C3—C2—C1 −0.9 (12)  C10—C15—C14—C13 1.2 (11)
C11—C10—C15—C14 0.1 (10)  C10—C9—C8—Se1 174.2 (4)
C9—C10—C15—C14 −178.5 (6)  N1—C9—C8—Se1 −63.2 (5)
C2—C3—C4—C5 −0.1 (13)  C13—C12—C11—C10 1.8 (13)
C5—C6—C1—C2 2.0 (10)  C15—C10—C11—C12 −1.7 (11)
C5—C6—C1—C7 −178.4 (6)  C9—C10—C11—C12 176.9 (7)
C3—C2—C1—C6 −0.1 (10)  C15—C14—C13—C12 −1.1 (12)
C3—C2—C1—C7 −179.7 (6)  C11—C12—C13—C14 0.4 (13)
C15—C10—C9—N1 145.4 (5)  C6—C1—C7—Se1 93.7 (6)
C11—C10—C9—N1 −33.1 (8)  C2—C1—C7—Se1 −86.7 (7)
C15—C10—C9—C8 −92.7 (6)  C3—C4—C5—C6 2.1 (13)
C11—C10—C9—C8 88.7 (7)  C1—C6—C5—C4 −3.1 (11)

Hydrogen-bond geometry (Å, °)

Cg is the centroid of the C1–C6 aromatic ring.

| D—H···A          | D—H  | H···A | D···A       | D—H···A |
|------------------|-------|-------|-------------|---------|
| N1—H1A···O4i     | 0.89  | 2.16  | 3.003 (7)   | 157     |
| N1—H1B···O4ii    | 0.89  | 2.05  | 2.893 (6)   | 159     |
| N1—H1C···O2iii   | 0.89  | 1.92  | 2.812 (6)   | 176     |
| O1—H1D···O2iv    | 0.85  | 1.91  | 2.726 (8)   | 161     |
| O1—H1E···O5v     | 0.85  | 1.95  | 2.730 (6)   | 152     |
| O3—H3A···O1      | 0.82  | 1.68  | 2.483 (9)   | 167     |
| C15—H15···Cgvi   | 0.93  | 2.75  | 3.547 (7)   | 144     |

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