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2,6-[Bis(dimethylamino)methyl]phenylselenenyl chloride/bromide monohydrate

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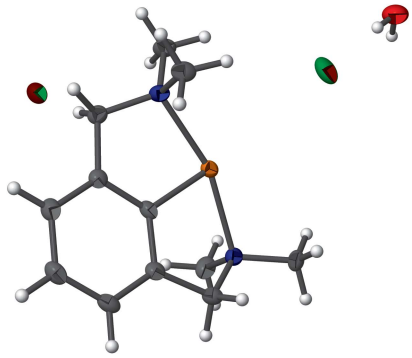
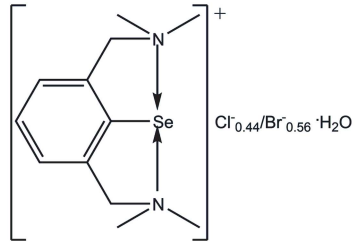
In the title hydrated salt, $C_{12}H_{19}N_2Se^+\cdot Cl_{0.44}/Br_{0.56}^-\cdot H_2O$, the halide ions (both with site symmetry 2) have different Cl^-/Br^- occupancies of 0.399 (2)/0.601 (2) and 0.491 (2)/0.509 (2). In the crystal, the cation and anion are linked by an Se$\cdots X$ (X = Cl/Br) interaction of length 3.5593 (8) Å. The water molecule and anions are linked by O—H$\cdots X$ hydrogen bonds into a staggered chain propagating in the b-axis direction and the packing is consolidated by weak C—H$\cdots X$ interactions.

3D view



Chemical scheme



Structure description

The molecular structure of hydrated molecular salt **3**, $[C_{12}H_{19}N_2Se]^+Cl_{0.44}/Br_{0.56}^-\cdot H_2O$ is shown in Fig. 1. It crystallizes in the monoclinic crystal system with 56% of Br and 46% of Cl in total but distributed over two sites in different ratios [in site 1, the Cl/Br ratio is 0.399 (2)/0.601 (2) and in site 2 the Cl/Br ratio is 0.491 (2)/0.509 (2)]. There have been three previous structures containing the same cation with PF_6^- (Fujihara *et al.*, 1995), HF_2^- (Poleschner & Seppelt, 2004) and Br^- (Varga *et al.*, 2010) as counter-ions. This latter compound is essentially isostructural with **3** but with a stoichiometric amount of Br^-.

The geometry around Se is T-shaped with an N1—Se—N2 angle of 161.38 (7)°. The Se—N bonds give rise to two five-membered chelate rings and the central ring (C1–C6) is essentially planar (r.m.s. deviation = 0.002 Å) with two other atoms approximately in this plane [Se1, 0.065 (2) Å and C7 0.059 (2) Å]. The N1—Se1—N2 axis is twisted by 14.4 (2)° about this plane. The Se—N bond lengths are 2.1836 (17) and 2.1861 (17) Å and the Se$\cdots$Br/Cl distance is 3.559 (3) Å, which is shorter than Σr_{vdw} (Se, X) 3.75/3.65 Å for Br/Cl, providing a second coordination sphere.

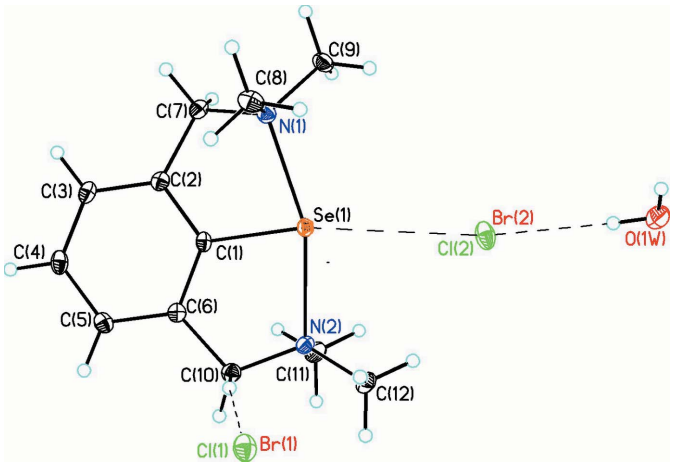


Figure 1
The molecular structure showing 30% displacement ellipsoids. Hydrogen bonds are shown as dashed lines.

In the extended structure, the water molecule and anions are linked by hydrogen bonds (Table 1) into a staggered chain in the *b*-axis direction. The packing also features weak C—H···Br interactions. In addition there are C—H···π interactions, which link the cations into dimers (shown in Fig. 2). The overall packing is shown in Fig. 3.

Synthesis and crystallization

To a stirred solution of **1** (1.25 g, 4.61 mmol) in dry Et_2O (15 ml) at 273 K, *n*-BuLi (2.88 ml, 4.60 mmol) was added dropwise *via* syringe under an inert argon atmosphere. After 30 min, the colour of the reaction mixture changed from colourless to yellowish, and elemental Se powder (0.36 g, 4.61 mmol) was added under a full flow of argon. After 6 h stirring at room temperature, saturated NH_4Cl (50 ml) was added and oxygen gas was bubbled for 20 min. The whole mixture was extracted with Et_2O and the organic phase was washed with H_2O, dried over Na_2SO_4 and concentrated by rotary evaporator. The reaction scheme is shown in Fig. 4. The resulting solid was dried over vacuum to afford **3** (0.94 g, 75% yield) as a yellowish solid (m.p. = 427–430 K). Colourless prisms of **3** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution at room temperature. The water molecule of crystallization was presumably absorbed from the atmosphere. ^{1}H NMR: δ (p.p.m.) 7.20 (*s*, 3H, $ArCH_2$), 4.12 (*s*, 4H, $-CH_2$), 2.91 (*s*, 12H, NCH_3). ^{13}C NMR: δ (p.p.m.) 132.57, 132.40, 128.42, 125.94, 64.04, 48.98. ^{77}Se NMR: δ (p.p.m.) 1201. Analysis calculated (%) for $C_{12}H_{19}Cl/BrSeN_2$: C 42.67; H 6.34; N 7.95. Found: C 42.52; H 6.34; N 8.26.

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

Cg is the centroid of the C1–C6 ring. *X*1 = Br1/Cl1; *X*2 = Br2/Cl2.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*2···*X*1^{i}	0.82 (2)	2.50 (2)	3.315 (2)	177 (4)
O1*W*—H1*W*1···*X*2	0.82 (2)	2.44 (2)	3.256 (2)	177 (3)
C7—H7*B*···Br1^{ii}	0.99	2.89	3.869 (2)	171
C7—H7*A*···*Cg*^{iii}	0.99	2.94	3.908 (3)	165

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

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The anions have refined site

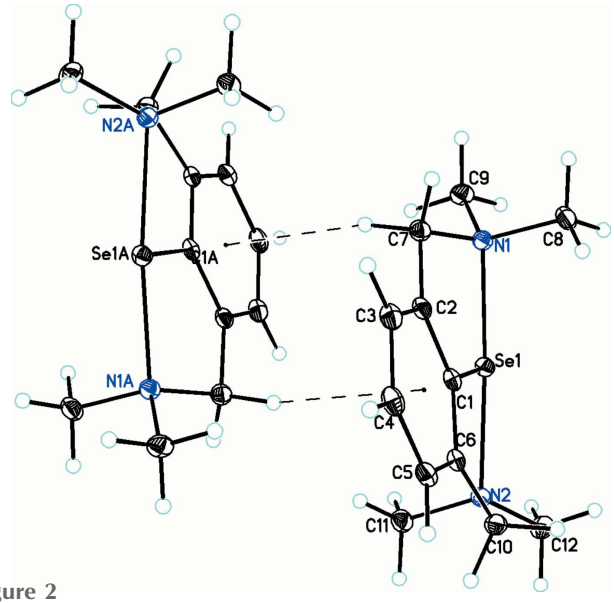


Figure 2
Diagram of a pair of cations showing the C—H···π interactions linking them into dimeric units. Atomic displacement parameters are at the 30% probability level.

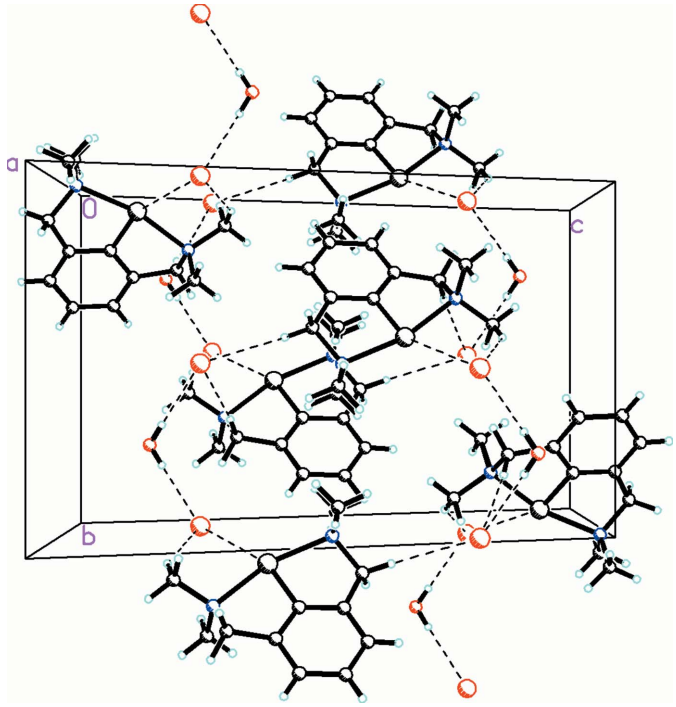


Figure 3
Packing diagram viewed along [100] showing O—H···Br and C—H···Br interactions generating a staggered chain in the [010] direction.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{19}N_2Se^+\cdot Cl_{0.44}/Br_{0.56}^-\cdot H_2O$
M_r	348.45
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	123
a, *b*, *c* (Å)	14.7635 (7), 11.2385 (3), 19.4113 (10)
β (°)	115.087 (6)
V (Å^3)	2916.9 (3)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	5.92
Crystal size (mm)	0.38 × 0.24 × 0.15
Data collection	
Diffractometer	Agilent Xcalibur, Ruby, Gemini
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2012). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.289, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6566, 2917, 2780
R_{int}	0.022
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.628
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.075, 1.09
No. of reflections	2917
No. of parameters	169
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.36

Computer programs: *CrysAlis PRO* (Agilent, 2012), *SHELXS97* and *SHELXTL* (Sheldrick, 2008) and *SHELXL2017/1* (Sheldrick, 2015).

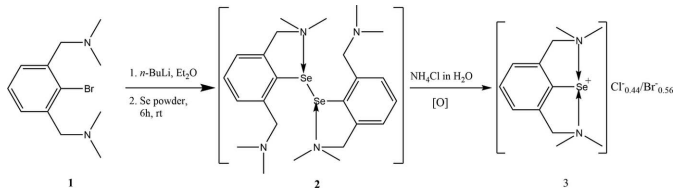


Figure 4
Reaction scheme.

occupancies of 0.399 (2)/0.601 (2) for Cl1/Br1 and 0.491 (2)/0.509 (2) for Cl2/Br2.

Funding information

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full crystallographic data

IUCrData (2017). **2**, x171634 [https://doi.org/10.1107/S2414314617016340]

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Crystal data

$C_{12}H_{19}N_2Se^+ \cdot Cl0.44/Br_{0.56}^- \cdot H_2O$
M_r = 348.45
Monoclinic, $C2/c$
a = 14.7635 (7) Å
b = 11.2385 (3) Å
c = 19.4113 (10) Å
β = 115.087 (6)°
V = 2916.9 (3) Å^3
Z = 8
$F(000)$ = 1408
D_x = 1.587 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 4254 reflections
θ = 5.0–75.3°
μ = 5.92 mm^{-1}
T = 123 K
Prism, colouress
0.38 × 0.24 × 0.15 mm

Data collection

Agilent Xcalibur, Ruby, Gemini diffractometer
Detector resolution: 10.5081 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Agilent, 2012). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min} = 0.289, T_{max} = 1.000
6566 measured reflections
2917 independent reflections
2780 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 75.4°, θ_{min} = 5.0°
h = −18→16
k = −14→9
l = −23→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.09
2917 reflections
169 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 1.6414P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

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

Refinement. The H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.95–0.99 Å. U_{iso}(H) = xU_{eq}(C), where x = 1.5 for methyl H atoms and 1.2 for all other C-bound H atoms. The hydrogen atoms attached to water were refined isotropically.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Se1	0.75366 (2)	0.43673 (2)	0.62278 (2)	0.01726 (10)	
Br1	0.500000	0.48925 (4)	0.750000	0.02635 (17)	0.601 (4)
Br2	1.000000	0.52385 (4)	0.750000	0.0332 (2)	0.509 (5)
Cl1	0.500000	0.48925 (4)	0.750000	0.02635 (17)	0.399 (4)
Cl2	1.000000	0.52385 (4)	0.750000	0.0332 (2)	0.491 (5)
N1	0.70609 (13)	0.51175 (15)	0.50884 (10)	0.0188 (3)	
N2	0.75927 (13)	0.32516 (15)	0.71661 (9)	0.0193 (3)	
O1W	1.12342 (16)	0.75325 (18)	0.84692 (10)	0.0373 (4)	
H1W1	1.091 (2)	0.696 (2)	0.8234 (18)	0.038 (9)*	
H1W2	1.092 (3)	0.811 (2)	0.824 (2)	0.053 (11)*	
C1	0.65376 (14)	0.32552 (16)	0.56659 (11)	0.0166 (4)	
C2	0.62026 (14)	0.32262 (17)	0.48798 (11)	0.0184 (4)	
C3	0.54910 (16)	0.23754 (18)	0.44704 (12)	0.0218 (4)	
H3A	0.525043	0.233201	0.393301	0.026*	
C4	0.51333 (16)	0.15873 (18)	0.48529 (13)	0.0233 (4)	
H4A	0.464577	0.101073	0.457183	0.028*	
C5	0.54826 (15)	0.16341 (17)	0.56450 (12)	0.0210 (4)	
H5A	0.523723	0.108918	0.589965	0.025*	
C6	0.61907 (15)	0.24827 (17)	0.60566 (12)	0.0174 (4)	
C7	0.66883 (15)	0.40967 (19)	0.45535 (11)	0.0207 (4)	
H7A	0.725058	0.371125	0.448937	0.025*	
H7B	0.619757	0.437687	0.404953	0.025*	
C8	0.62515 (17)	0.5973 (2)	0.49817 (13)	0.0259 (4)	
H8A	0.601274	0.633182	0.447481	0.039*	
H8B	0.650705	0.659832	0.536903	0.039*	
H8C	0.569814	0.555742	0.503041	0.039*	
C9	0.79051 (16)	0.57326 (19)	0.50219 (13)	0.0239 (4)	
H9A	0.768046	0.606851	0.451002	0.036*	
H9B	0.844699	0.516366	0.511282	0.036*	
H9C	0.814757	0.637367	0.539886	0.036*	
C10	0.65818 (16)	0.27041 (18)	0.68983 (12)	0.0212 (4)	
H10A	0.612571	0.324523	0.700279	0.025*	
H10B	0.662383	0.194509	0.716907	0.025*	
C11	0.83732 (17)	0.2335 (2)	0.73130 (13)	0.0259 (4)	
H11A	0.841875	0.183212	0.773882	0.039*	
H11B	0.901881	0.272361	0.743994	0.039*	
H11C	0.819892	0.184354	0.685755	0.039*	
C12	0.78343 (18)	0.3997 (2)	0.78520 (12)	0.0265 (4)	
H12A	0.785606	0.349623	0.827207	0.040*	
H12B	0.731980	0.461028	0.774246	0.040*	
H12C	0.848667	0.437680	0.799471	0.040*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.01777 (14)	0.01528 (13)	0.01697 (13)	−0.00190 (7)	0.00566 (9)	−0.00137 (7)
Br1	0.0248 (2)	0.0202 (2)	0.0300 (2)	0.000	0.00769 (17)	0.000
Br2	0.0205 (3)	0.0250 (3)	0.0441 (3)	0.000	0.0038 (2)	0.000
Cl1	0.0248 (2)	0.0202 (2)	0.0300 (2)	0.000	0.00769 (17)	0.000
Cl2	0.0205 (3)	0.0250 (3)	0.0441 (3)	0.000	0.0038 (2)	0.000
N1	0.0184 (8)	0.0187 (8)	0.0194 (8)	0.0009 (6)	0.0080 (6)	0.0018 (6)
N2	0.0236 (8)	0.0171 (7)	0.0156 (7)	0.0002 (7)	0.0069 (6)	−0.0005 (6)
O1W	0.0454 (11)	0.0365 (10)	0.0249 (8)	−0.0029 (8)	0.0100 (8)	0.0004 (7)
C1	0.0145 (8)	0.0120 (7)	0.0197 (9)	0.0010 (7)	0.0039 (7)	−0.0019 (7)
C2	0.0175 (9)	0.0161 (8)	0.0193 (9)	0.0040 (7)	0.0056 (7)	0.0011 (7)
C3	0.0197 (9)	0.0204 (9)	0.0196 (9)	0.0028 (8)	0.0027 (8)	−0.0026 (7)
C4	0.0197 (9)	0.0166 (9)	0.0280 (10)	−0.0001 (7)	0.0047 (8)	−0.0044 (8)
C5	0.0212 (9)	0.0143 (8)	0.0271 (10)	0.0010 (7)	0.0100 (8)	0.0011 (7)
C6	0.0173 (9)	0.0141 (8)	0.0202 (9)	0.0033 (7)	0.0075 (8)	0.0002 (7)
C7	0.0218 (9)	0.0205 (9)	0.0175 (9)	0.0021 (8)	0.0061 (7)	0.0003 (7)
C8	0.0274 (10)	0.0197 (9)	0.0338 (11)	0.0069 (9)	0.0160 (9)	0.0066 (8)
C9	0.0213 (10)	0.0251 (10)	0.0276 (10)	−0.0031 (8)	0.0126 (8)	0.0035 (8)
C10	0.0246 (10)	0.0194 (9)	0.0197 (9)	−0.0010 (8)	0.0096 (8)	0.0001 (7)
C11	0.0268 (11)	0.0256 (10)	0.0225 (10)	0.0060 (9)	0.0078 (9)	0.0022 (8)
C12	0.0340 (11)	0.0263 (10)	0.0185 (9)	−0.0039 (9)	0.0104 (8)	−0.0058 (8)

Geometric parameters (Å, º)

Se1—C1	1.8875 (19)	C5—C6	1.390 (3)
Se1—N2	2.1836 (17)	C5—H5A	0.9500
Se1—N1	2.1861 (17)	C6—C10	1.505 (3)
N1—C9	1.478 (3)	C7—H7A	0.9900
N1—C8	1.479 (3)	C7—H7B	0.9900
N1—C7	1.487 (3)	C8—H8A	0.9800
N2—C11	1.480 (3)	C8—H8B	0.9800
N2—C12	1.483 (3)	C8—H8C	0.9800
N2—C10	1.489 (3)	C9—H9A	0.9800
O1W—H1W1	0.818 (18)	C9—H9B	0.9800
O1W—H1W2	0.819 (18)	C9—H9C	0.9800
C1—C6	1.386 (3)	C10—H10A	0.9900
C1—C2	1.391 (3)	C10—H10B	0.9900
C2—C3	1.393 (3)	C11—H11A	0.9800
C2—C7	1.503 (3)	C11—H11B	0.9800
C3—C4	1.395 (3)	C11—H11C	0.9800
C3—H3A	0.9500	C12—H12A	0.9800
C4—C5	1.400 (3)	C12—H12B	0.9800
C4—H4A	0.9500	C12—H12C	0.9800
C1—Se1—N2	81.13 (8)	N1—C7—H7A	110.1
C1—Se1—N1	80.42 (8)	C2—C7—H7A	110.1

N2—Se1—N1	161.38 (7)	N1—C7—H7B	110.1
C9—N1—C8	110.17 (17)	C2—C7—H7B	110.1
C9—N1—C7	112.08 (17)	H7A—C7—H7B	108.4
C8—N1—C7	111.48 (17)	N1—C8—H8A	109.5
C9—N1—Se1	110.34 (13)	N1—C8—H8B	109.5
C8—N1—Se1	106.65 (13)	H8A—C8—H8B	109.5
C7—N1—Se1	105.89 (12)	N1—C8—H8C	109.5
C11—N2—C12	110.41 (17)	H8A—C8—H8C	109.5
C11—N2—C10	111.28 (17)	H8B—C8—H8C	109.5
C12—N2—C10	111.76 (17)	N1—C9—H9A	109.5
C11—N2—Se1	108.14 (13)	N1—C9—H9B	109.5
C12—N2—Se1	109.52 (13)	H9A—C9—H9B	109.5
C10—N2—Se1	105.55 (12)	N1—C9—H9C	109.5
H1W1—O1W—H1W2	105 (3)	H9A—C9—H9C	109.5
C6—C1—C2	122.94 (18)	H9B—C9—H9C	109.5
C6—C1—Se1	118.56 (15)	N2—C10—C6	108.28 (16)
C2—C1—Se1	118.48 (15)	N2—C10—H10A	110.0
C1—C2—C3	118.25 (19)	C6—C10—H10A	110.0
C1—C2—C7	115.85 (17)	N2—C10—H10B	110.0
C3—C2—C7	125.84 (19)	C6—C10—H10B	110.0
C2—C3—C4	119.73 (19)	H10A—C10—H10B	108.4
C2—C3—H3A	120.1	N2—C11—H11A	109.5
C4—C3—H3A	120.1	N2—C11—H11B	109.5
C3—C4—C5	120.94 (19)	H11A—C11—H11B	109.5
C3—C4—H4A	119.5	N2—C11—H11C	109.5
C5—C4—H4A	119.5	H11A—C11—H11C	109.5
C6—C5—C4	119.61 (19)	H11B—C11—H11C	109.5
C6—C5—H5A	120.2	N2—C12—H12A	109.5
C4—C5—H5A	120.2	N2—C12—H12B	109.5
C1—C6—C5	118.53 (19)	H12A—C12—H12B	109.5
C1—C6—C10	115.46 (17)	N2—C12—H12C	109.5
C5—C6—C10	125.89 (19)	H12A—C12—H12C	109.5
N1—C7—C2	108.02 (16)	H12B—C12—H12C	109.5

N2—Se1—C1—C6	11.53 (15)	C2—C1—C6—C10	−175.68 (17)
N1—Se1—C1—C6	−165.94 (16)	Se1—C1—C6—C10	6.2 (2)
N2—Se1—C1—C2	−166.72 (16)	C4—C5—C6—C1	−0.6 (3)
N1—Se1—C1—C2	15.81 (14)	C4—C5—C6—C10	175.25 (19)
C6—C1—C2—C3	−0.4 (3)	C9—N1—C7—C2	154.58 (17)
Se1—C1—C2—C3	177.74 (15)	C8—N1—C7—C2	−81.4 (2)
C6—C1—C2—C7	−177.69 (18)	Se1—N1—C7—C2	34.21 (17)
Se1—C1—C2—C7	0.5 (2)	C1—C2—C7—N1	−25.4 (2)
C1—C2—C3—C4	0.3 (3)	C3—C2—C7—N1	157.57 (19)
C7—C2—C3—C4	177.24 (19)	C11—N2—C10—C6	−82.82 (19)
C2—C3—C4—C5	−0.3 (3)	C12—N2—C10—C6	153.24 (17)
C3—C4—C5—C6	0.5 (3)	Se1—N2—C10—C6	34.26 (17)
C2—C1—C6—C5	0.6 (3)	C1—C6—C10—N2	−28.9 (2)
Se1—C1—C6—C5	−177.58 (14)	C5—C6—C10—N2	155.18 (19)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*2···X1^{i}	0.82 (2)	2.50 (2)	3.315 (2)	177 (4)
O1*W*—H1*W*1···X2	0.82 (2)	2.44 (2)	3.256 (2)	177 (3)
C7—H7*B*···Br1^{ii}	0.99	2.89	3.869 (2)	171
C7—H7*A*···*Cg*^{iii}	0.99	2.94	3.908 (3)	165

Symmetry codes: (i) *x*+1/2, *y*+1/2, *z*; (ii) *x*+3/2, *y*+3/2, *z*+1; (iii) −*x*+3/2, −*y*+1/2, −*z*+1.