Data collection: *CAD-4 VAX/PC Software* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 VAX/PC Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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N,N'-Diphenylguanidinium Hydrogenselenite Monohydrate

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## Abstract

In the crystal structure of the title compound, $C_{13}H_{14}N_3^+.HSeO_3^-.H_2O$, the phenyl rings lie *syn* to the

unsubstituted N atom of the cation and the geometry of the guanidinium group is close to that expected for a central C_{sp^2} atom. The crystal packing is stabilized by an extensive network of hydrogen bonds. The anion is an acceptor of the N—H guanidinium groups and the water molecule forms a four-membered hydrogen-bonded ring with the anion.

Comment

The title compound belongs to a series of new selenite compounds of organic moieties synthesized as part of a project to study new materials with potentially interesting optical and dielectric properties (de Matos Gomes *et al.*, 1995; Paixão *et al.*, 1997). Selenite compounds are particularly interesting due to the fact that they often exhibit ferro- or antiferroelectric properties and structural phase transitions at low temperature associated with the onset of the polar phases, as found in the alkali trihydrogenselenites (Shulalov, Ivanov, Gordeeva & Kirpichnikova, 1970). Phase transitions have been observed in the novel compound benzyltrimethylammonium trihydrogen selenite (de Matos Gomes *et al.*, 1995), but DSC measurements failed to show any peculiar feature for the present compound while cooling from room temperature down to 233 K.

(I)
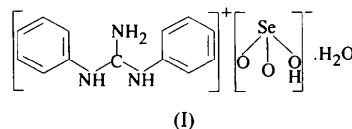
The $HSeO_3^-$ ion is pyramidal with two shorter Se—O bonds [1.649 (2) and 1.665 (2) Å] and one longer Se—OH bond [1.768 (2) Å]. The average value of an Se—O bond is 1.65 Å and that of an Se—OH bond is about 1.75 Å (Chomnilpan, Liminga, Sonneveld & Visser, 1981). The O—Se—O angles, 99–105°, are in the same range as those observed in other hydrogenselenite and trihydrogen selenite compounds (Chomnilpan, Tellgren & Liminga, 1978). The geometry of the inorganic moiety, namely the presence of the two short Se—O bond distances, clearly implies that the diphenylguanidinine molecule is protonated.

Regarding the geometry of the *N,N'*-diphenylguanidinium cation (dpgH$^+$) it is pertinent to make a comparison with a similar compound, *N,N'*-diphenylguanidinium *m*-chlorobenzeneseleninate (Antolini *et al.*, 1991). Also relevant for discussion are the structures of *N*-adamant-1-yl-*N'*-(2-iodophenyl)guanidinium chloride (Weakley, Scherz & Keana, 1990), of the unprotonated molecules of *N,N'*-diphenylguanidine (dpg) (Zakharov, Andrianov & Struchkov, 1980) and of *N,N'*-bis(2-methylphenyl)guanidine (Brown & Gash, 1984).

The bond lengths C1—N1 [1.342 (4) Å] and C1—N3 [1.335 (4) Å] of the guadininium group are close to the standard value of a delocalized C=N bond [1.339 (5) Å]
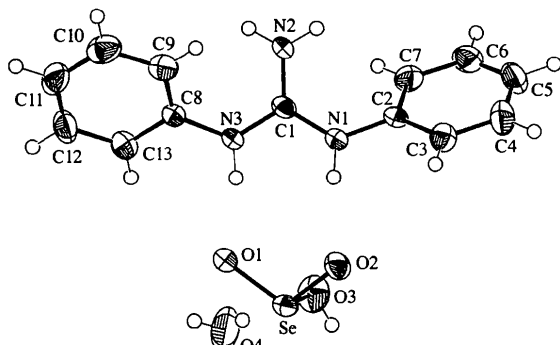
Fig. 1. *ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level except for H atoms which are given arbitrary radii.

observed in the *m*-chlorobenzeneseleninate dpgH⁺ salt. In the molecular crystal of dpg, the dihedral angles are 75.2 and 92.4° for the two independent molecules. These differences in conformation reflect the low barrier of rotation of the phenyl rings (Zakharov *et al.*, 1980).

The crystal packing (Fig. 2) is stabilized by an extensive network of hydrogen bonds. The guanidinium N atoms act as donors towards the bare O1 and O2 atoms of the anion, each O atom being an acceptor in two hydrogen bonds. These hydrogen bonds form an infinite three-dimensional network. The water molecule and the anion form a four-membered cooperative hydrogen-bonded ring through the scheme O4—H17···O3—H18···O4^i—H17^i···O3^i—H18^i···O4 [symmetry code: (i) $1-x$, $-y$, $-z$].

while the bond length C1—N2 [1.317 (4) Å] is somewhat shorter. These distances are comparable with the average values relevant to guanidinium cations such as 1.321 and 1.328 Å for unsubstituted and substituted species, respectively (Allen *et al.*, 1987). The bond lengths of the guanidinium group are close to those expected for a central C_{sp^2} atom. The geometry is similar to that observed in the dpgH⁺ *m*-chlorobenzeneseleninate salt and other guanidinium salts, but differs from that of unprotonated dpg, where one shorter bond of double character and two larger single bonds are observed [C1—N3 1.288 (7), 1.288 (7); C1—N1 1.359 (8), 1.383 (7); C1—N2 1.350 (8), 1.351 (8) Å, for the two independent molecules, respectively]. Thus, the free base in the crystal state has two H atoms bonded to N2, one bonded to N1 and none to N3. The geometry of *N,N'*-bis(2-methylphenyl)guanidine reported by Brown & Gash (1984) is somewhat unusual in that the C1—N2 bond is larger [1.382 (4) Å] than the other bonds [C1—N1 1.364 (4) and C1—N3 1.365 (4) Å] which was interpreted as due to the bonding of three H atoms to N2 while N1 and N3 would lack primary bonded H atoms.

The bond lengths N1—C2 and N3—C8 are somewhat shorter than the standard bond length of an sp^2 N—C bond but close to the values found in the molecular crystal of diphenylguanidine (Zakharov, Andrianov & Struchkov, 1980) and in diphenyl formazane (Omel'chenko, Kondrashov, Ginzburg & Neigauz, 1974). The phenyl rings are practically flat and have the usual geometry: mean values of the C—C bond length 1.379 (4) Å and C—C—C valence angle 120.0 (5)°. The rings lie *syn* to the unsubstituted N atom (N2), similarly to the geometry of *N*-adamant-1-yl-*N'*-(2-iodophenyl)guanidinium chloride, while in both the free base and in the *m*-chlorobenzeneseleninate salt one of the rings lies *syn* and the other *anti*. The dihedral angle between the central planar guanidine fragment N₃C and the least-squares planes of the phenyl rings are 45.74 (13) (C2–C7) and 48.35 (15)° (C8–C13). The dihedral angle between the planes of the two phenyl rings is 88.21 (11)°, compared with an angle of 94.7°
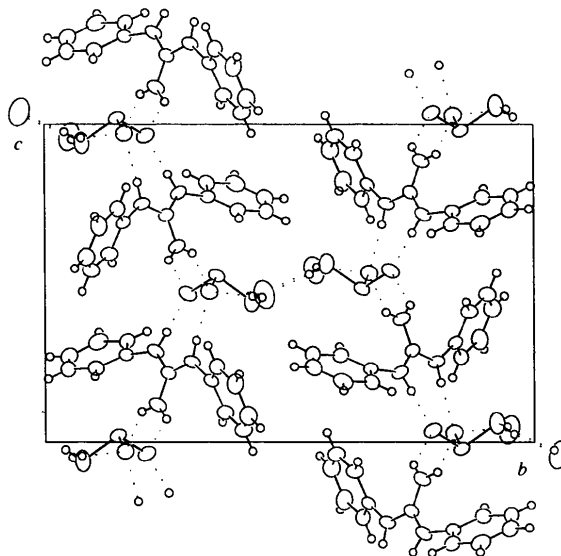

Fig. 2. Packing diagram viewed down the *a* axis, showing the hydrogen-bonding scheme.

Experimental

The title compound was synthesized by reaction of 1 mmol of diphenylguanidine (Merck, 99.9% purity) in a water/methanol (1:1) solution with selenious acid, prepared from 99.9% pure SeO_2. Crystals suitable for X-ray experiments were obtained by slow evaporation from the solution after 3 d.

Crystal data

$C_{13}H_{14}N_3^+ \cdot HSeO_3^- \cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 358.26$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 6.360 (1)$ Å	$\theta = 9.8–15.8°$
$b = 19.272 (2)$ Å	$\mu = 2.454$ mm^{-1}
$c = 12.604 (2)$ Å	$T = 293 (2)$ K
$\beta = 93.75 (1)°$	Plate
$V = 1541.6 (4)$ Å^3	$0.30 \times 0.30 \times 0.10$ mm
$Z = 4$	Colourless
$D_x = 1.544$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	1844 reflections with $I > 2\sigma(I)$
Profile data from ω–2θ scans	$R_{int} = 0.046$
Absorption correction:	$\theta_{max} = 35.0°$
ψ scan (North, Phillips & Mathews, 1968)	$h = -6 \rightarrow 8$
	$k = -26 \rightarrow 31$
$T_{min} = 0.56$, $T_{max} = 0.78$	$l = -9 \rightarrow 20$
6572 measured reflections	3 standard reflections
3157 independent reflections	frequency: 180 min
	intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.081$
$S = 1.060$
3157 reflections
198 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 1.3453P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.421$ e Å^{-3}
$\Delta\rho_{min} = -0.342$ e Å^{-3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0048 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Se—O1	1.649 (2)	N1—C2	1.413 (4)
Se—O2	1.665 (2)	N3—C1	1.335 (4)
Se—O3	1.768 (2)	N3—C8	1.417 (4)
N1—C1	1.342 (4)	N2—C1	1.317 (4)
O1—Se—O2	104.62 (11)	N2—C1—N1	121.9 (3)
O1—Se—O3	98.94 (12)	N3—C1—N1	116.6 (3)
O2—Se—O3	99.02 (12)	C3—C2—N1	117.8 (3)
C1—N1—C2	127.2 (3)	C7—C2—N1	122.9 (3)
C1—N3—C8	127.4 (3)	C9—C8—N3	122.9 (3)
N2—C1—N3	121.5 (3)	C13—C8—N3	117.4 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2	0.86 (3)	2.01	2.868 (3)	173
N3—H2$\cdots$O1	0.86 (4)	1.86	2.698 (3)	166
N2—H14$\cdots$O2^i	0.86 (4)	2.15	2.909 (3)	147
N2—H15$\cdots$O1^{ii}	0.86 (4)	2.10	2.780 (3)	136
O4—H16$\cdots$O2^{iii}	0.69 (6)	2.06 (6)	2.731 (4)	163 (7)
O4—H17$\cdots$O3	0.55 (7)	2.26 (7)	2.799 (5)	172 (9)
O3—H18$\cdots$O4^{iv}	0.82 (10)	1.96	2.756 (5)	162

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

The structure was solved by direct methods. H atoms of the organic moiety were placed at calculated positions and refined as riding using the SHELXL93 (Sheldrick, 1993) defaults. The position of the H atom of the HSeO$_3^-$ anion was determined from a difference Fourier synthesis and then the angle H—O—Se refined keeping a fixed H—O distance of 0.82 Å. The H atoms of the water molecule were located from a difference Fourier synthesis and refined with an isotropic displacement parameter of $1.5U_{eq}$ of the parent O atom. Examination of the crystal structure with PLATON (Spek, 1995) showed that there are no additional solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

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