

Dimethyl selenoxide

Alexander S. Filatov, Eric Block and Marina A. Petrukhina*

Department of Chemistry, University at Albany, SUNY, Albany, NY 12222, USA
Correspondence e-mail: marina@albany.edu

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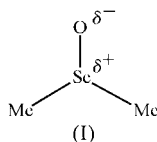
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The title molecule, C_2H_6OSe , has a trigonal–pyramidal structure analogous to that of its sulfur analog, dimethyl sulfoxide (DMSO). The Se–O distance in dimethyl selenoxide (DMSeO) is 1.6756 (16) Å [*versus* S–O of 1.531 (5) Å in DMSO], consistent with a highly polar σ bond. In the solid state, the molecules of DMSeO are linked into centrosymmetric dimers formed by two C–H \cdots O hydrogen bonds. These dimers further aggregate into a ladder-like supramolecular network *via* two additional intermolecular C–H \cdots O interactions. As a result, each O atom of DMSeO acts as an acceptor of three hydrogen bonds.

Comment

Dimethyl selenoxide (DMSeO) is of interest because of its biological activity and redox cycling (Lanfear *et al.*, 1994; Goeger & Ganter, 1994; Bray *et al.*, 2001), its role in the global selenium cycle (Rael *et al.*, 1996; Zhang *et al.*, 1999; Zhang & Frankenberger, 2000), and its excellent hydrogen-bond acceptor properties, which are superior to those of dimethyl sulfoxide (DMSO; Renault & Le Questel, 2004). Also of interest is the proper description of the chalcogen–oxygen bonds in DMSeO and DMSO, which can be treated as single polar bonds or as double bonds involving *d* orbitals (Bartell *et al.*, 1970; Mezey & Haas, 1982; Dobado *et al.*, 1999; Chesnut & Quin, 2004). We present here the first X-ray structural characterization of dimethyl selenoxide, (I), revealing its geometry and solid-state packing. The latter is notable for involving aggregates held together by three C–H hydrogen bonds to each O atom, which is consistent with a highly polar $Se^+–O^-$ bond with three lone pairs on the O atom.



Similar to DMSO, the molecule of DMSeO exhibits a trigonal–pyramidal shape (Fig. 1), with a mean Se–C distance of 1.931 (3) Å, an Se–O distance of 1.6756 (16) Å, a mean C–Se–O angle of 103.0 (3)° and an C–Se–C angle of

95.95 (10)° (Table 1). The sum of the angles about the Se atom, Σ_{X-Se-Y} (*ca* 302°), is less than the expected value for pyramidal trisubstituted selenium with one lone pair (*ca* 328.5°) and less than the analogous value for DMSO (*ca* 311°; Thomas *et al.*, 1966). Consequently, the pyramid formed with the O atom and two C atoms as a base and the S atom as an apex in the DMSO molecule is considerably flatter than that in DMSeO. The perpendicular distance from the apical chalcogen atom to the basal plane is 0.8383 (12) Å in DMSeO *versus* only 0.706 Å in the DMSO molecule. This difference can mostly be attributed to the influence of the chalcogen lone pair size (*4d versus 3d*) on the final shape of the molecule.

A search of the Cambridge Structural Database (CSD; Version 5.26 of February 2005; Allen, 2002) revealed 15 crystal structures of different selenoxides. The Se–O and Se–C bond lengths are very similar within this class of compounds, and lie in the ranges 1.621–1.690 and 1.907–1.958 Å, respectively. The introduction of electron-withdrawing perfluorinated substituents into the molecule results in shortening of the Se–O and Se–C bond lengths (Gockel *et al.*, 2000; Klapotke *et al.*, 2002). It is also informative to compare the Se–O distances in $(CH_3)_2SeO$ with $(CH_3)_2SeO_2$ (dimethyl selenone, DMSeO₂), which is the oxidized form of (I). The distance in DMSeO₂ [1.626 (1) Å; Dikarev, Becker *et al.*, 2003] is 0.05 Å shorter than that in dimethyl selenoxide [1.6756 (16) Å; Table 1]. This observation is consistent with the fact that the Se–O bond in selenoxides is weaker than that in selenones.

Recent high-level calculations showed that the bonding to the central Se atom is consistent with a model of a highly polarized Se–O σ bond rather than an Se=O double bond, the bond strength depending mainly on electrostatic interactions (Dobado *et al.*, 1999). These calculations on DMSeO at the B3LYP and at the MP2(full) (values in parentheses) levels, using the 6-311+G* basis set, predict Se–O = 1.672 Å (1.663 Å), C–Se = 1.983 Å (1.948 Å), C–Se–O = 104.0° (103.8°) and C–Se–C = 94.4° (93.8°), Σ_{X-Se-Y} being approximately 302° (301°). Our X-ray structural data show a very good agreement with the geometrical values obtained from calculations.

We have recently presented the first example of dimethyl selenoxide coordinated to the dirhodium(II,II) tetra(trifluoroacetate) complex (Dikarev, Petrukhina *et al.*, 2003). The first approximation of the DMSeO geometry has been based on the observed fact (Cotton *et al.*, 2001) that the selected metal complex does not significantly alter the structural

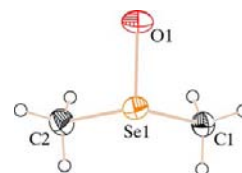


Figure 1

The molecule of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

parameters of coordinated ligands. Our predictions based on the X-ray study of the dimethyl selenoxide complex ($\text{Se}-\text{O} = 1.70 \text{ \AA}$, $\text{Se}-\text{C} = 1.92 \text{ \AA}$ and $\Sigma_{\text{X-Se-Y}} = 301^\circ$) are in good agreement with the data presented here for uncomplexed DMSeO. This result proves the great potential of the proposed adduct-formation technique for retrieving geometric information for compounds that are liquids or low-melting solids, or for compounds that resist providing crystalline samples suitable for X-ray diffraction studies.

In the crystal structure of (I) (Fig. 2), the DMSeO molecules form centrosymmetric dimers *via* two pairs of $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2). These dimers are further linked through two additional intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds to form ladder-like chains that do not interpenetrate each other. Atoms C1 and O1 in the title molecule at (x, y, z) act as a hydrogen-bond donor and acceptor, respectively, to atoms O1 and C1 in the molecule at $(-x, 1-y, 1-z)$, thus generating a centrosymmetric dimer centered at $(0, \frac{1}{2}, \frac{1}{2})$. Moreover, atoms C1 and C2 at (x, y, z) both act as hydrogen-bond donors to atom O1 in the molecule at $(x+1, y, z)$, thus producing a chain running parallel to the [100] direction and generated by translation. The DMSeO molecules that form dimers lie in two different chains, related to each other by inversion.

It is worth stressing that the formation of three hydrogen bonds by one O atom in the solid-state structure of (I) supports the model of a strongly polarized $\text{Se}-\text{O}$ σ bond; similar formation of multiple hydrogen bonds to an O atom was also seen in the solid-state structure of DMSO (Thomas *et al.*, 1966). Alternatively, a selenium–oxygen double bond would be much less likely to lead to the observed intermolecular aggregation of the DMSeO molecules (Fig. 2), but would rather result in separate chains. Thus, our structural study provides additional verification of a larger contribution of the polarized $\text{Se}-\text{O}$ σ bond to the resonance hybrid of DMSeO.

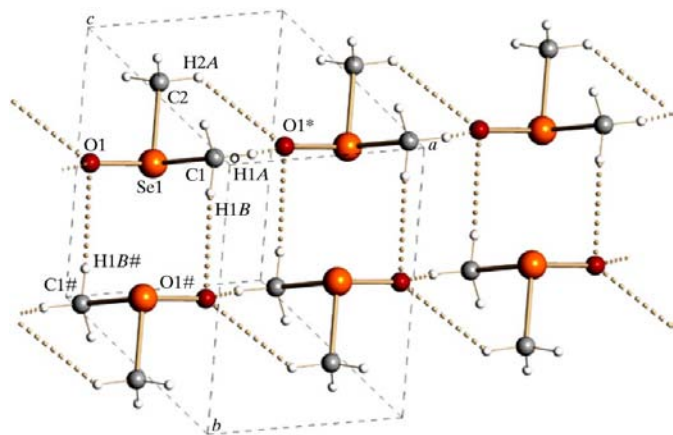


Figure 2

A fragment of the crystal structure of (I), showing the formation of a ladder-like chain along the [100] direction through $\text{Csp}^3-\text{H}\cdots\text{O}$ hydrogen bonds. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x+1, y, z)$ and $(-x, 1-y, 1-z)$, respectively.

Experimental

Dimethyl selenoxide was synthesized as described previously (Dikarev, Petrukhina *et al.*, 2003). The solid was dissolved in *n*-hexane; the solution was then filtered and kept at 258 K, affording colorless crystals after 2 d. DMSeO decomposes before reaching the melting point (m.p. 365–366 K, sealed capillary). Our attempts to sublime DMSeO at 333 K or higher temperatures resulted in the decomposition of the material. Sublimation at lower temperatures provided an amorphous powder that was not suitable for X-ray analysis. The thermal degradation reaction of DMSeO in the presence of rhodium(II) trifluoroacetate in the gas phase at 403–413 K led to entrapment of the dimethyl selenide fragment in the form of its metal complex (Dikarev, Petrukhina *et al.*, 2003). [For a prior report of the gas phase decomposition of DMSeO, see Rael *et al.* (1996).]

Crystal data

$\text{C}_2\text{H}_6\text{OSe}$	$Z = 2$
$M_r = 125.03$	$D_x = 2.063 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 4.9794 (7) \text{ \AA}$	Cell parameters from 1564 reflections
$b = 6.1470 (9) \text{ \AA}$	$\theta = 3.1\text{--}28.1^\circ$
$c = 6.8905 (10) \text{ \AA}$	$\mu = 9.11 \text{ mm}^{-1}$
$\alpha = 106.850 (2)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 90.177 (2)^\circ$	Plate, colorless
$\gamma = 94.213 (2)^\circ$	$0.26 \times 0.17 \times 0.05 \text{ mm}$
$V = 201.24 (5) \text{ \AA}^3$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	895 independent reflections
ω scans	849 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.012$
$T_{\text{min}} = 0.182$, $T_{\text{max}} = 0.632$	$\theta_{\text{max}} = 28.1^\circ$
1735 measured reflections	$h = -6 \rightarrow 6$
	$k = -7 \rightarrow 7$
	$l = -8 \rightarrow 9$

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.026P]$
$wR(F^2) = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} < 0.001$
895 reflections	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
61 parameters	$\Delta\rho_{\text{min}} = -0.52 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Se1—O1	1.6756 (16)	Se1—C1	1.932 (2)
Se1—C2	1.930 (2)		
O1—Se1—C2	103.11 (9)	C2—Se1—C1	95.95 (10)
O1—Se1—C1	102.79 (9)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
C1—H1A \cdots O1 ⁱ	0.95 (3)	2.49 (3)	3.238 (3)	135 (2)
C1—H1B \cdots O1 ⁱⁱ	0.93 (3)	2.54 (3)	3.457 (3)	169 (2)
C2—H2A \cdots O1 ⁱ	0.95 (3)	2.53 (3)	3.272 (3)	135 (3)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x, -y+1, -z+1$.

The range of the refined C—H distances is 0.92 (3)–0.97 (3) \AA for the methyl groups.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1528). Services for accessing these data are described at the back of the journal.

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