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2,2'-Diselenodibenzoic acid *N,N*-dimethylformamide disolvate

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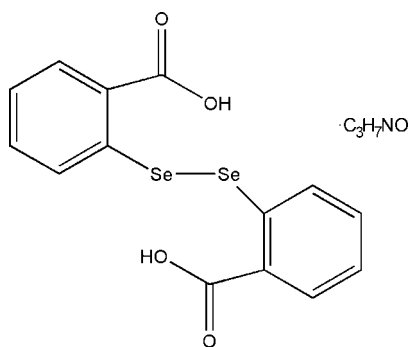
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å;
R factor = 0.034; wR factor = 0.091; data-to-parameter ratio = 14.9.

The molecular structure of the title compound, $\text{C}_{14}\text{H}_{10}\text{O}_4\text{Se}_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$, reveals C_i symmetry, with the inversion centre located at the mid-point of the Se—Se bond. Diselenide derivatives are important in the synthesis of ebselen and other organoselenium compounds. These derivatives are of interest owing to their biological activity as oxidoreductants. The structure displays an O—H...O hydrogen bond between the carboxyl group and the carbonyl unit of the dimethylformamide solvent molecule.

Related literature

For related literature, see: Israelachvili (1991); Iwaoka & Tomoda (1994); Mughesh *et al.* (2001); Nagao *et al.* (1998); Zade *et al.* (2005); Fujita *et al.* (1997); Björnstedt *et al.* (1995); Sagher *et al.* (2006).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{10}\text{O}_4\text{Se}_2 \cdot 2\text{C}_3\text{H}_7\text{NO}$ $a = 8.202$ (2) Å
 $M_r = 546.34$ $b = 13.223$ (4) Å
 Monoclinic, $C2/c$ $c = 21.849$ (6) Å

$\beta = 96.425$ (4)°
 $V = 2354.6$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 3.18$ mm⁻¹
 $T = 293$ (2) K
 $0.30 \times 0.20 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer 4745 measured reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996) 2072 independent reflections
 $T_{\min} = 0.449$, $T_{\max} = 0.569$ 1607 reflections with $I > 2\sigma(I)$
 (expected range = 0.418–0.530) $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$ 139 parameters
 $wR(F^2) = 0.091$ H-atom parameters constrained
 $S = 1.08$ $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 2072 reflections $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1}-\text{H1} \cdots \text{O3}^i$	0.82	1.73	2.541 (4)	169

Symmetry code: (i) $x + 1, y + 1, z$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2145).

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supplementary materials

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Comment

During the past decade the non-bonded interactions (Mugesh *et al.*, 2001) and their role in molecular recognition, conformational transformation, and molecular packing in crystals were studied (Israelachvili, 1991). In particular, for organoselenium derivatives have been frequently discovered that the divalent selenium interacts with a nearby hetero-atom (O, N, Se) generating a pseudo-high-valent selenium species. The weak actions have been successfully applied not only to asymmetric synthesis (Fujita *et al.*, 1997) but also to enzyme-mimetic catalytic reactions. Moreover, previous experiments indicated that a pseudo-multivalent state of Se might be related to biological activities of Se compounds (Iwaoka & Tomoda, 1994). The seleno compounds can serve as oxidoreductants with the methionine sulfoxide reductase enzymes (Sagher *et al.*, 2006) and as reducing agents for lipid hydroperoxides (Björnstedt *et al.*, 1995). This phenomenon attracts considerable attention (Nagao *et al.*, 1998).

Many kinds of diselenide compounds and their derivatives have been synthesized and fully characterized successfully, but the structure of the title compound (I) has not been investigated thoroughly. In this paper, the titled compound was synthesized and characterized by NMR spectra. In the title molecule, the Se—Se bond distance is 2.287 Å, and the distance (2.703 Å) of Se and nearby O atom of carbonyl are significantly shorter than the sum of their vander waals radii (3.40 Å) (Zade *et al.*, 2005). The crystal structure involves hydrogen bond O—H...O between the carboxyl group and carbonyl moiety of a solvate (Table 1). distance 2.541 (4) Å and angle is 169°. The asymmetric unit is planar with r.m.s. deviation of 0.030 Å. The dihedral angle between these symmetry related planar moieties is 83.60°.

Experimental

Absolute ethanol (30 ml), dried by distillation over sodium, was added with magnetic stirring to 1.0 g (12.6 mmol) of selenium and 0.35 g (9.3 mmol) of sodium borohydride cooled on an ice bath. After the initial reaction had subsided, the mixture was stirred and heated at reflux for 1.5 h with N₂ introduced into the liquid in order to dissolve the selenium and expel H₂Se. Cooled on an ice bath again, diazonium salt (8.4 mmol) prepared from anthranilic acid was added and the solution was refluxed for 3 h. O₂ was passed through the mixture slowly for 1.5 h to remove any H₂Se. After acidification with hydrochloric acid, the filter cake was dissolved in sodium acid carbonate solution and reflux for 1 h, then acidified with hydrochloric acid again. The pale-yellow solid product was collected by filtration and recrystallized from DMF-methanol (2: 1). Yield: 85%, ¹H NMR (DMSO-*d*₆) δ: 8.20 (d, 2 H), 7.64 (d, 2 H), 7.50 (t, 2 H), 7.38 (t, 2 H); ¹³C NMR (DMSO-*d*₆) δ: 123.2, 124.8, 127.0, 128.5, 131.3, 131.9, 166.9 (C=O); ⁷⁷Se NMR (DMSO-*d*₆) δ: 439.2. Anal. Calcd. for: C₁₄H₁₀O₄Se₂, C, 42.02; H, 2.52% Found: C, 41.58; H, 2.49%.

Refinement

(type here to add refinement details)

Figures

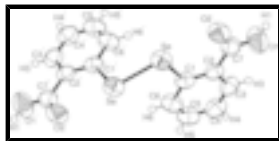


Fig. 1. The molecular structure of the title compound. The solvent molecules have been omitted.

2,2'-Diselenodibenzoic acid *N,N*-dimethylformamide disolvate

Crystal data

$C_{14}H_{10}O_4Se_2 \cdot 2C_3H_7NO$

$M_r = 546.34$

Monoclinic, $C2/c$

Hall symbol: $-C2yc$

$a = 8.202$ (2) Å

$b = 13.223$ (4) Å

$c = 21.849$ (6) Å

$\beta = 96.425$ (4)°

$V = 2354.6$ (11) Å³

$Z = 4$

$F_{000} = 1096$

$D_x = 1.541$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1983 reflections

$\theta = 2.9$ – 27.3 °

$\mu = 3.18$ mm⁻¹

$T = 293$ (2) K

Block, yellow

$0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

ω scans

Absorption correction: Multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.449$, $T_{\max} = 0.569$

4745 measured reflections

2072 independent reflections

1607 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 25.0$ °

$\theta_{\min} = 1.9$ °

$h = -9 \rightarrow 8$

$k = -14 \rightarrow 15$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.091$

$S = 1.08$

2072 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2 + 1.4577P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

$\Delta\rho_{\max} = 0.41$ e Å⁻³

139 parameters

$$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Se	1.03742 (4)	0.89916 (3)	0.303005 (16)	0.06579 (17)
N	0.3833 (4)	0.0067 (3)	0.60861 (14)	0.0774 (9)
O1	1.0166 (5)	0.7946 (3)	0.49575 (13)	0.1180 (12)
H1	1.0792	0.8286	0.5193	0.177*
O2	1.1015 (3)	0.89762 (19)	0.42617 (12)	0.0793 (7)
O3	0.2003 (5)	-0.1147 (3)	0.57969 (15)	0.1173 (12)
C1	0.9004 (4)	0.7933 (2)	0.33137 (16)	0.0568 (8)
C2	0.9069 (4)	0.7714 (2)	0.39329 (16)	0.0591 (8)
C3	0.8061 (4)	0.6957 (3)	0.41283 (18)	0.0735 (10)
H3	0.8099	0.6813	0.4546	0.088*
C4	0.7014 (5)	0.6421 (3)	0.3715 (2)	0.0815 (11)
H4	0.6346	0.5918	0.3849	0.098*
C5	0.6972 (5)	0.6636 (3)	0.3109 (2)	0.0829 (12)
H5	0.6268	0.6272	0.2827	0.099*
C6	0.7950 (4)	0.7384 (3)	0.28949 (18)	0.0719 (10)
H6	0.7901	0.7518	0.2475	0.086*
C7	1.0173 (5)	0.8280 (3)	0.44022 (17)	0.0698 (10)
C8	0.2838 (5)	-0.0414 (4)	0.5669 (2)	0.0895 (12)
H8	0.2762	-0.0195	0.5262	0.107*
C9	0.3944 (6)	-0.0226 (4)	0.67189 (18)	0.1087 (17)
H9A	0.3579	0.0321	0.6958	0.163*
H9B	0.5062	-0.0388	0.6863	0.163*
H9C	0.3265	-0.0808	0.6760	0.163*
C10	0.4853 (6)	0.0882 (4)	0.5917 (2)	0.1167 (17)
H10A	0.5978	0.0666	0.5958	0.175*
H10B	0.4740	0.1451	0.6182	0.175*
H10C	0.4523	0.1074	0.5498	0.175*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se	0.0719 (3)	0.0463 (2)	0.0776 (3)	-0.01384 (16)	0.00154 (18)	-0.00285 (16)
N	0.0660 (19)	0.084 (2)	0.080 (2)	0.0075 (17)	0.0005 (17)	-0.0035 (18)
O1	0.139 (3)	0.143 (3)	0.0727 (18)	-0.073 (2)	0.0137 (18)	-0.0099 (19)
O2	0.0797 (17)	0.0727 (18)	0.0833 (17)	-0.0342 (14)	-0.0008 (14)	-0.0056 (13)
O3	0.124 (3)	0.134 (3)	0.093 (2)	-0.037 (2)	0.012 (2)	-0.016 (2)
C1	0.0492 (17)	0.0408 (17)	0.079 (2)	-0.0040 (14)	0.0027 (15)	-0.0056 (15)
C2	0.0502 (18)	0.052 (2)	0.076 (2)	-0.0037 (15)	0.0092 (16)	-0.0096 (16)
C3	0.071 (2)	0.066 (2)	0.086 (2)	-0.0155 (19)	0.0219 (19)	-0.005 (2)
C4	0.071 (2)	0.065 (2)	0.111 (3)	-0.024 (2)	0.021 (2)	-0.012 (2)
C5	0.071 (2)	0.066 (3)	0.108 (3)	-0.022 (2)	-0.007 (2)	-0.014 (2)
C6	0.071 (2)	0.057 (2)	0.085 (2)	-0.0136 (18)	-0.0061 (19)	-0.0070 (18)
C7	0.067 (2)	0.070 (3)	0.073 (2)	-0.0101 (19)	0.0106 (18)	-0.0080 (19)
C8	0.083 (3)	0.108 (4)	0.078 (3)	-0.010 (3)	0.008 (2)	-0.002 (3)
C9	0.117 (4)	0.139 (5)	0.067 (3)	0.033 (3)	-0.008 (2)	-0.010 (3)
C10	0.087 (3)	0.106 (4)	0.153 (5)	-0.011 (3)	-0.001 (3)	0.008 (3)

Geometric parameters (\AA , $^\circ$)

Se—C1	1.940 (3)	C3—H3	0.9300
Se—Se ⁱ	2.3288 (9)	C4—C5	1.350 (5)
N—C8	1.317 (5)	C4—H4	0.9300
N—C9	1.429 (5)	C5—C6	1.388 (5)
N—C10	1.438 (5)	C5—H5	0.9300
O1—C7	1.292 (4)	C6—H6	0.9300
O1—H1	0.8200	C8—H8	0.9300
O2—C7	1.211 (4)	C9—H9A	0.9600
O3—C8	1.236 (5)	C9—H9B	0.9600
C1—C2	1.379 (5)	C9—H9C	0.9600
C1—C6	1.391 (4)	C10—H10A	0.9600
C2—C3	1.396 (5)	C10—H10B	0.9600
C2—C7	1.491 (5)	C10—H10C	0.9600
C3—C4	1.372 (5)		
C1—Se—Se ⁱ	102.72 (10)	C5—C6—H6	120.3
C8—N—C9	120.4 (4)	C1—C6—H6	120.3
C8—N—C10	121.2 (4)	O2—C7—O1	124.1 (4)
C9—N—C10	118.4 (4)	O2—C7—C2	121.8 (3)
C7—O1—H1	109.5	O1—C7—C2	114.1 (3)
C2—C1—C6	119.3 (3)	O3—C8—N	122.5 (4)
C2—C1—Se	120.3 (2)	O3—C8—H8	118.7
C6—C1—Se	120.4 (3)	N—C8—H8	118.7
C1—C2—C3	119.5 (3)	N—C9—H9A	109.5
C1—C2—C7	121.6 (3)	N—C9—H9B	109.5
C3—C2—C7	119.0 (3)	H9A—C9—H9B	109.5
C4—C3—C2	121.2 (4)	N—C9—H9C	109.5

C4—C3—H3	119.4	H9A—C9—H9C	109.5
C2—C3—H3	119.4	H9B—C9—H9C	109.5
C5—C4—C3	118.8 (4)	N—C10—H10A	109.5
C5—C4—H4	120.6	N—C10—H10B	109.5
C3—C4—H4	120.6	H10A—C10—H10B	109.5
C4—C5—C6	121.9 (4)	N—C10—H10C	109.5
C4—C5—H5	119.0	H10A—C10—H10C	109.5
C6—C5—H5	119.0	H10B—C10—H10C	109.5
C5—C6—C1	119.3 (4)		

Symmetry codes: (i) $-x+2, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O3 ⁱⁱ	0.82	1.73	2.541 (4)	169

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

Fig. 1

