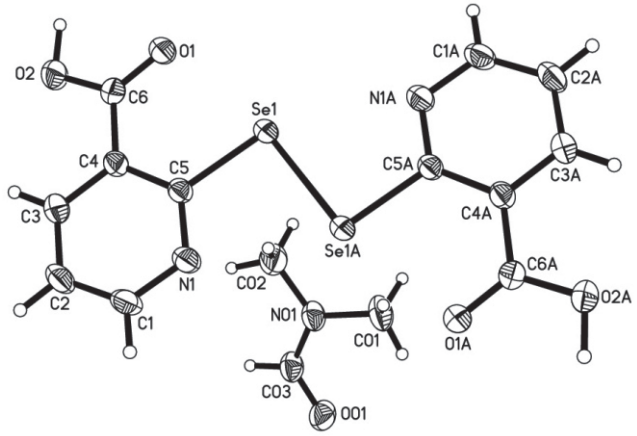
Crystal structure 2,2'-diselanediyldibenzoic acid — dimethylformamide (1/2), $C_{18}H_{22}N_4O_6Se_2$

De-Zhong Niu[*, I], Lin Yao[II] and Yuwei Zhang[III]

[I] College of Chemistry & Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou 221116, Jiangsu Province, P. R. China
[II] Zhengzhou University, The College of Chemistry and Molecular Engineering, Zhengzhou 450002, Henan Province, P. R. China
[III] Zhengzhou Yihe Hospital Clinical Trial Research Center, Zhengzhou 450047, Henan Province, P. R. China

Received January 13, 2015, accepted June 15, 2015, available online June 25, 2015, CCDC no. 1267/4342



Abstract

$C_{18}H_{22}N_4O_6Se_2$, monoclinic, $P2_1/c$ (no. 14), a = 7.3648(4) Å, b = 15.2480(7) Å, c = 9.9280(5) Å, β = 101.311(3)°, V = 1093.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.0230, $wR_{ref}(F^2)$ = 0.0602, T = 296 K.

Table 1. Data collection and handling.

Crystal:	yellow needles, size 0.20×0.28×0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	34.24 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ and ω
$2\theta_{max}$:	55.82°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9945, 2593
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2105
$N(param)_{refined}$:	136
Programs:	SHELX [9]

Source of material

A two-step method was used for preparation of the title compound: firstly, the synthesis of disodium diselenide in ice water can be achieved under nitrogen atmosphere due to the reduction effect of $NaBH_4$ (6.5 g, 170 mmol, 50 mL H_2O) to selenium (6.0 g, 75 mmol, 50 mL H_2O). Secondly, the chlorine atom in 2-chloropyridine-3-carboxylic acid (11.8 g, 76 mmol, 70 mL H_2O) was substituted by freshly prepared disodium diselenide, resulting in the formation of 2-(2-(3-carboxypyridin-2-yl)diselanyl)-pyridine-3-carboxylic acid (*DSPA*). The obtained *DSPA* material was filtrated following by treatments of Na_2CO_3 and HCl, and was further washed with H_2O and EtOH. Pure *DSPA* can be obtained by recrystallization in *n*-hexane. Yellow needle used for the single crystal structure data collection were prepared through recrystallization of the precipitate in *N,N*-dimethylformamide.

IR (KBr, cm^{-1}): 3103(m), 2911(w), 2781(w), 2466(w), 1878(m), 1712(m), 1600(m), 1560(s), 1455(s), 1369(s), 1287(s), 1232(w), 1158(s), 1073(s), 1005(s), 899(m), 864(s), 764(s), 727(s), 666(s).

Discussion

Recently, organic selenium compounds have attracted attention due to their unique properties and wide applications in organic synthesis, pharmaceutics, anti-contamination, antiseptic, antiviral, especially in the field of anti-tumor therapy [1–3]. In the title crystal structure, the compound has two six-membered rings. The dihedral angle between these rings is 0°, which is completely different to 2-(2-(pyridin-2-yl)diselanyl)pyridine-1-oxide (85.76°) [4]. The dihedral angle of Se1A–Se1–C5–N1 and Se1A–Se1–C5–C4 are 1.69° and –177.76°, respectively. The Se–Se single bond distance is 2.383 Å, a value which is in good agreement with those reported in the literature [5–7], and shorter than of compounds: $[C_{13}H_{11}NSe_2]$ (2.533 Å) [2] and $[(pyridine)_8Yb_4(SeSe)_2(Se)_2(\mu_2\text{-}SPh)_2(SPh)_2$ (2.598 Å)] [8]. The bond length of Se–C is 1.921 Å, similar to that found in $[C_{13}H_{11}NSe_2]$ (1.937 Å) [2]. In the carboxylic acid groups the two O–C bond length are 1.216 Å and 1.316 Å, respectively. Each title molecules donates two hydrogen bonds by its OH groups to the oxygen atoms of two adjacent DMF molecules (d(O2–H2···O01^{i}) = 2.574(2) Å (symmetry code i: 2–x, –½+y, ½–z).

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*e*	0.8433	–0.1021	0.5749	0.092
H(1A)	4*e*	0.4556	0.2519	0.2121	0.065
H(3A)	4*e*	0.6899	0.1148	0.5385	0.062
H(2A)	4*e*	0.5673	0.2459	0.4435	0.069
H(02A)	4*e*	1.0532	0.1449	0.1431	0.112
H(02B)	4*e*	1.0655	0.0647	0.0465	0.112
H(02C)	4*e*	0.8717	0.1006	0.0632	0.112
H(03A)	4*e*	1.1178	0.2707	0.0549	0.068
H(01A)	4*e*	0.9255	0.1895	–0.2566	0.102
H(01B)	4*e*	0.7897	0.1289	–0.1956	0.102
H(01C)	4*e*	0.9844	0.0935	–0.2111	0.102

* Correspondence author (e-mail: xzsd_ndz@263.net)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se(1)	4*e*	0.56530(3)	–0.04276(1)	0.09801(2)	0.0528(1)	0.0311(1)	0.0375(1)	–0.00062(8)	0.00449(8)	–0.00360(7)
O(1)	4*e*	0.7102(2)	–0.10420(9)	0.3465(1)	0.085(1)	0.0407(8)	0.0420(7)	0.0055(7)	0.0008(7)	–0.0020(6)
O(2)	4*e*	0.7980(2)	–0.03870(9)	0.5491(2)	0.085(1)	0.0549(9)	0.0384(7)	0.0086(8)	–0.0021(7)	–0.0029(6)
N(1)	4*e*	0.5039(2)	0.1310(1)	0.1657(2)	0.0570(9)	0.0358(9)	0.0475(9)	0.0018(8)	0.0027(7)	–0.0047(7)
C(4)	4*e*	0.6459(3)	0.0460(1)	0.3618(2)	0.044(1)	0.038(1)	0.0399(9)	–0.0046(8)	0.0077(7)	–0.0051(7)
C(6)	4*e*	0.7206(3)	–0.0389(1)	0.4178(2)	0.053(1)	0.044(1)	0.0369(9)	–0.0024(9)	0.0077(8)	0.0001(8)
C(5)	4*e*	0.5718(2)	0.0549(1)	0.2212(2)	0.0402(9)	0.034(1)	0.0390(9)	–0.0033(7)	0.0079(7)	–0.0042(7)
C(1)	4*e*	0.5041(3)	0.1991(1)	0.2501(2)	0.064(1)	0.033(1)	0.062(1)	0.0065(9)	0.005(1)	–0.005(1)
C(3)	4*e*	0.6429(3)	0.1187(1)	0.4447(2)	0.063(1)	0.048(1)	0.041(1)	–0.003(1)	0.0053(9)	–0.0095(9)
C(2)	4*e*	0.5708(3)	0.1966(1)	0.3890(2)	0.072(1)	0.040(1)	0.059(1)	0.000(1)	0.011(1)	–0.017(1)
O(01)	4*e*	1.0768(2)	0.3080(1)	–0.1263(2)	0.092(1)	0.065(1)	0.0504(8)	–0.0230(9)	0.0028(8)	–0.0022(8)
N(01)	4*e*	0.9957(2)	0.1754(1)	–0.0544(2)	0.056(1)	0.060(1)	0.0453(9)	–0.0133(9)	0.0093(7)	–0.0121(8)
C(02)	4*e*	0.9966(4)	0.1165(2)	0.0591(2)	0.097(2)	0.069(2)	0.059(1)	–0.027(2)	0.021(1)	–0.008(1)
C(03)	4*e*	1.0685(3)	0.2542(2)	–0.0350(2)	0.060(1)	0.065(2)	0.044(1)	–0.013(1)	0.0058(9)	–0.011(1)
C(01)	4*e*	0.9172(3)	0.1442(2)	–0.1909(2)	0.072(1)	0.079(2)	0.053(1)	–0.021(1)	0.013(1)	–0.024(1)

Acknowledgments. This work was supported by Natural Science Foundation of Xuzhou city government (grant nos. XM12D082 and XX12A020).

References

1. Buasin, K. K.; Jaspreet S.: A novel and convenient synthesis towards 2-pyridylselenium compounds: X-ray crystal structure of 4,4'-dimethyl-2,2'-dipridyl diselenide and tris(2-pyridylseleno)methane. J. Organ. Chem. **658** (2002) 71–76.
2. Debasish, M.; Govindasamy, M.: Regioselective deiodination of thyroxine by iodothyronine deiodinase mimics: An unusual mechanistic pathway involving cooperative chalcogen and halogen bonding. J. Am. Chem. Soc. **134** (2012)4269–4279.
3. Shigeyuki, F.; Hiroyuki, Y.; Yutaka, Y.: Development of a novel antidiabetic zinc complex with an organoselenium ligand at the lowest dosage in KK-Ay mice. J. Inorg. Biochem. **121** (2013) 10–15.
4. Ma. D. L.; Gao, M. X.; Zhang, H. J.; Shen, Z.; Niu, D. Z.: Syntheses and crystal structures of $(PySe)_2$ and $Bi_2(PySe)_6$ (HPySe = 2-Pyridineselenol N-Oxide). Chin. J. Struct. Chem. **29** (2010) 444–448.
5 Poleschner, H.; Ellrodt, S.; Malischewski, M.; Nakatsuji, J. Y.; Rohner, C.; Seppelt, K.: $Trip_2C_6H_3SeF$: the first isolated selenenyl fluoride. Angew. Chem. Int. Ed. Engl. **51** (2012) 419–422.
6. Sangit, K.; Karuppasamy, K.; Harkesh, B. S.; Gotthelf, W.; Ray, J. B.: Chelate ring size effect on the reactivity of [2-(2-phenyl-5,6-dihydro-4*H*-1,3-oxazinyl)] lithium and Se···N interactions in low-valent organoselenium compounds: Facile isolation of diorganotriselenide. Organometallics. 23 (2004) 4199–4208.
7. Bani, K. S.; Debasish, M.; Mao, M.; Govindasamy, M.: Synthesis, structure, spirocyclization mechanism, and glutathione peroxidase-like antioxidant activity of stable spirodiazaselenurane and spirodiazatellurane. J. Am. Chem. Soc. **132** (2010) 5364–5374.
8. Anna, Y. K.; Thomas, J. E.; John, G. B.: Chalcogen-rich lanthanide clusters: Cluster reactivity and the influence of ancillary ligands on structure. J. Am. Chem. Soc. **123** (2001) 11933–11939.
9. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.