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Crystal structure of 1-butyl-2,3-dimethylimidazolium *O,Se*-dimethyl selenophosphate, $[C_9H_{17}N_2][C_2H_6O_3PSe]$, *a new ionic liquid*

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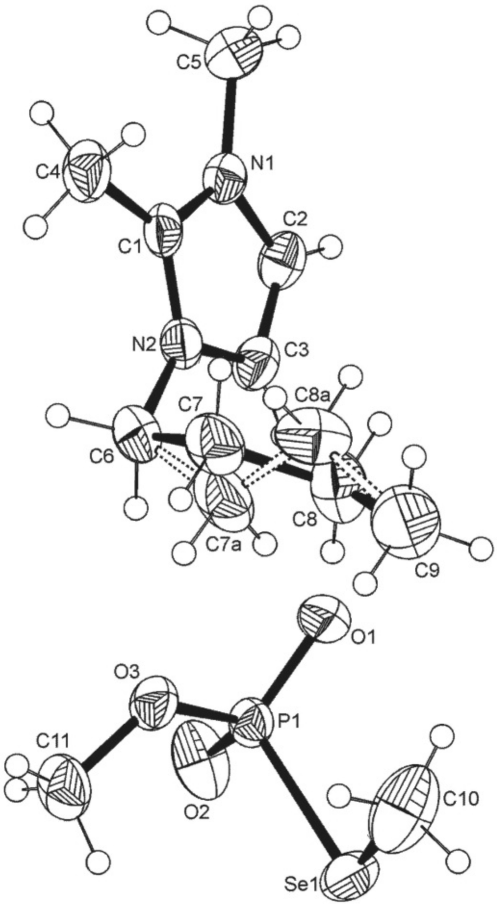

Abstract

$C_{11}H_{23}N_2O_3PSe$, triclinic, $P\overline{1}$ (no. 2), $a = 7.1451(2)$ Å, $b = 8.5754(3)$ Å, $c = 14.0997(6)$ Å, $\alpha = 73.547(2)°$, $\beta = 80.983(2)°$, $\gamma = 75.553(2)°$, $V = 798.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.040$, $wR_{ref}(F^2) = 0.096$, $T = 233$ K.

Source of material

The title compound was prepared from *O,O,O*-trimethyl selenophosphate [1] and 1-butyl-2,3-dimethylimidazolium chloride in acetonitrile. The volatiles (solvent and resulting chloromethane) were removed, and single crystals were collected from the dry residue (m.p. 23-24 °C).

^{1}H and ^{13}C NMR data are available in the CIF file.

Discussion

Recently, 1-butyl-3-methylimidazolium *O,Se*-dimethyl phosphoroselenoate has been introduced as a new ionic liquid for the dissolution of ligno-cellulosic materials [2]. The thermal stability of this solvent, however, was found to be less than satisfactory. Therefore, we prepared the corresponding 2-methyl derivative which was assumed to exhibit improved stability and readiness to crystallization.

In the crystal structure of the title compound, the butyl chain exhibits 2:1 positional disorder with regard to the atoms C7/C7A and C8/C8A. In the figure, the major component is depicted with full bonds, whereas the minor component with dashed bonds. Both components adopt *gauche* conformations (torsion angles N2–C6–C7–C8 and N2–C6–C7A–C8A: –65° and 55°, respectively). This situation is not uncommon for imidazolium salts with freely moving alkyl chains. Similar disorder has been observed in crystal structures of 1-butyl-3-methylimidazolium salts [3-7]. Other kinds of disorder involving different atoms of the butyl group have also been reported [7-12]. Replacement of one methoxy group in a dimethyl phosphate [13,14] by a methylseleno group reduces the symmetry of the anion. Hence, the central P atom of the *O,Se*-dimethyl phosphoroselenoate displays distorted tetrahedral geometry with angles ranging from 103.4° (∠O3–P1–Se1) to 120.7° (∠O1–P1–O2), as previously described for the sodium salt [15]. Again, the angle ∠P1–Se1–C10 = 97.7° is considerably smaller than the angle ∠P1–O3–C11 = 120.0°, and the low symmetry of the anion can also be seen in the different bond lengths d(P1—O3) = 1.609 Å and d(P1—Se1) = 2.244 Å, respectively. As a consequence, the melting point of this new salt is significantly lower than that of the corresponding dimethyl phosphate (54 °C) [16]. The imidazolium cation is coordinated by five anions with short C–H···O distances: C3–H···O1 (d(H···acceptor) = 2.23 Å and d(donor···acceptor) = 3.161 Å, ∠donor–H···acceptor = 170°), C6–H···O3 (2.56 Å and 3.537 Å, 174°), C4–H···O2^{i} (2.37 Å and 3.192 Å, 143°), C4–H···O1^{ii} (2.53 Å and 3.436 Å, 157°), C6–H···O1^{ii} (2.48 Å and 3.462 Å, 175°), C2–H···O1^{iii} (2.59Å and 3.386 Å, 142°), C2–H···O2^{iii} (2.64 Å and 3.438 Å, 144°), C5–H···O2^{iii} (2.69 Å and 3.595 Å, 156°), and C5–H···O3^{iv} (2.51 Å and 3.393 Å, 152°). Symmetry codes: i: $1+x,-1+y,z$; ii: $1+x,y,z$; iii: $1-x,-y,1-z$; iv: $2-x,-y,1-z$.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.28 × 0.32 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	24.53 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	49.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4595, 2763
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2389
$N(param)_{refined}$:	186
Programs:	SHELXS-97, SHELXL-97 [17]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	2*i*		0.7621	−0.2075	0.4733	0.058
H(3)	2*i*		0.6741	−0.0886	0.6170	0.057
H(4A)	2*i*		1.3692	−0.3858	0.6258	0.089
H(4B)	2*i*		1.3466	−0.2056	0.6408	0.089
H(4C)	2*i*		1.4013	−0.2360	0.5333	0.089
H(5A)	2*i*		1.2486	−0.2837	0.3949	0.100
H(5B)	2*i*		1.0708	−0.3630	0.3948	0.100
H(5C)	2*i*		1.2295	−0.4563	0.4706	0.100
H(10A)	2*i*		0.3112	−0.1307	0.8917	0.147
H(10B)	2*i*		0.2038	−0.0950	0.9930	0.147
H(10C)	2*i*		0.4045	−0.0428	0.9514	0.147
H(11A)	2*i*		0.5534	0.4290	0.7521	0.098
H(11B)	2*i*		0.6899	0.3029	0.8317	0.098
H(11C)	2*i*		0.4618	0.3400	0.8571	0.098
H(6A)	2*i*	0.67	0.8672	−0.0174	0.7347	0.070
H(6B)	2*i*	0.67	1.0974	−0.0635	0.7196	0.070

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(7A)	2*i*	0.67	1.0018	−0.2301	0.8769	0.078
H(7B)	2*i*	0.67	1.0898	−0.3514	0.8066	0.078
H(8A)	2*i*	0.67	0.6764	−0.2202	0.8292	0.090
H(8B)	2*i*	0.67	0.7788	−0.3708	0.7817	0.090
H(9A)	2*i*	0.67	0.6415	−0.4683	0.9411	0.151
H(9B)	2*i*	0.67	0.7711	−0.3831	0.9835	0.151
H(9C)	2*i*	0.67	0.8697	−0.5336	0.9357	0.151
H(6A1)	2*i*	0.33	1.1161	−0.1307	0.7388	0.070
H(6A2)	2*i*	0.33	0.9308	0.0144	0.7140	0.070
H(7A1)	2*i*	0.33	0.7352	−0.1460	0.8014	0.095
H(7A2)	2*i*	0.33	0.8954	−0.1496	0.8675	0.095
H(8A1)	2*i*	0.33	1.0440	−0.4201	0.8622	0.084
H(8A2)	2*i*	0.33	0.8992	−0.4174	0.7869	0.084
H(9A1)	2*i*	0.33	0.7919	−0.5565	0.9509	0.151
H(9A2)	2*i*	0.33	0.6338	−0.3929	0.9126	0.151
H(9A3)	2*i*	0.33	0.7783	−0.3955	0.9877	0.151

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se(1)	2*i*		0.14720(5)	0.16183(6)	0.86140(3)	0.0473(2)	0.0907(4)	0.0662(3)	−0.0218(2)	0.0140(2)	−0.0383(2)
P(1)	2*i*		0.3568(1)	0.1926(1)	0.72466(6)	0.0433(5)	0.0476(5)	0.0394(4)	−0.0169(4)	−0.0036(3)	−0.0140(4)
O(1)	2*i*		0.4014(3)	0.0415(3)	0.6879(2)	0.053(1)	0.065(2)	0.063(2)	−0.019(1)	0.005(1)	−0.036(1)
O(2)	2*i*		0.2750(5)	0.3566(3)	0.6603(2)	0.099(2)	0.054(2)	0.070(2)	−0.026(2)	−0.039(2)	0.003(1)
O(3)	2*i*		0.5545(3)	0.1921(3)	0.7660(2)	0.041(1)	0.067(2)	0.056(1)	−0.021(1)	−0.003(1)	−0.023(1)
N(1)	2*i*		1.0456(4)	−0.2601(3)	0.5091(2)	0.047(2)	0.042(1)	0.044(2)	−0.018(1)	0.002(1)	−0.008(1)
N(2)	2*i*		0.9702(4)	−0.1542(3)	0.6344(2)	0.041(1)	0.039(1)	0.052(2)	−0.015(1)	−0.005(1)	−0.013(1)
C(1)	2*i*		1.1182(4)	−0.2288(4)	0.5815(2)	0.041(2)	0.032(2)	0.054(2)	−0.016(1)	−0.004(1)	−0.005(1)
C(2)	2*i*		0.8478(5)	−0.2022(4)	0.5159(2)	0.041(2)	0.058(2)	0.047(2)	−0.018(2)	−0.009(1)	−0.006(2)
C(3)	2*i*		0.7997(4)	−0.1370(4)	0.5939(3)	0.035(2)	0.049(2)	0.056(2)	−0.012(1)	−0.004(1)	−0.009(2)
C(4)	2*i*		1.3268(5)	−0.2674(5)	0.5967(3)	0.040(2)	0.049(2)	0.090(3)	−0.011(2)	−0.012(2)	−0.014(2)
C(5)	2*i*		1.1582(6)	−0.3482(5)	0.4362(3)	0.068(2)	0.072(3)	0.063(2)	−0.025(2)	0.018(2)	−0.026(2)
C(10)	2*i*		0.2837(8)	−0.0535(7)	0.9333(4)	0.091(4)	0.121(4)	0.067(3)	−0.043(3)	−0.012(2)	0.020(3)
C(11)	2*i*		0.5658(6)	0.3270(5)	0.8049(3)	0.069(2)	0.077(3)	0.066(2)	−0.030(2)	−0.017(2)	−0.026(2)
C(6)	2*i*	0.67	0.9798(6)	−0.1062(5)	0.7256(3)	0.063(2)	0.059(2)	0.066(2)	−0.025(2)	−0.004(2)	−0.027(2)
C(7)	2*i*	0.67	0.982(1)	−0.260(1)	0.8175(6)	0.080(5)	0.074(6)	0.053(4)	−0.024(4)	−0.015(4)	−0.025(4)
C(8)	2*i*	0.67	0.785(1)	−0.318(1)	0.8338(5)	0.093(6)	0.072(5)	0.066(4)	−0.036(4)	−0.014(4)	−0.009(4)
C(9)	2*i*	0.67	0.7650(9)	−0.4358(7)	0.9319(4)	0.134(5)	0.106(4)	0.074(3)	−0.053(4)	0.011(3)	−0.029(3)
C(6A)	2*i*	0.33	0.9798(6)	−0.1062(5)	0.7256(3)	0.063(2)	0.059(2)	0.066(2)	−0.025(2)	−0.004(2)	−0.027(2)
C(7A)	2*i*	0.33	0.873(3)	−0.187(2)	0.812(1)	0.12(2)	0.08(1)	0.062(9)	−0.05(1)	−0.00(1)	−0.035(9)
C(8A)	2*i*	0.33	0.911(3)	−0.375(2)	0.843(1)	0.09(1)	0.053(8)	0.051(7)	0.011(8)	−0.010(7)	−0.004(6)
C(9A)	2*i*	0.33	0.7650(9)	−0.4358(7)	0.9319(4)	0.134(5)	0.106(4)	0.074(3)	−0.053(4)	0.011(3)	−0.029(3)

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