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Bis(1-ethyl-3-methylimidazolium) 3,6-diselanylidene-1,2,4,5-tetraselena-3,6-diphosphacyclohexane-3,6-diselenolate

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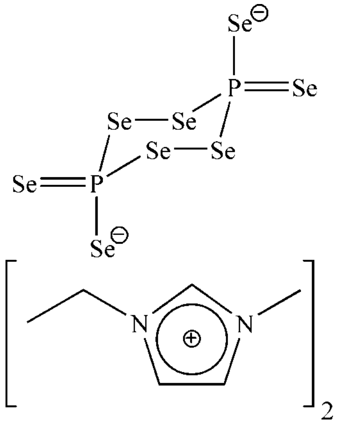
Key indicators: single-crystal X-ray study; *T* = 293 K; mean σ(C–C) = 0.007 Å; *R* factor = 0.029; *wR* factor = 0.063; data-to-parameter ratio = 31.5.

In the title compound, $2C_6H_{11}N_2^+\cdot P_2Se_8^{2-}$ or $[EMIM]_2P_2Se_8$ (EMIM = 1-ethyl-3-methylimidazolium), the anions, located about inversion centers between EMIM cations, exhibit a cyclohexane-like chair conformation. The cations are found in columns along the *a* axis, with centroid–centroid distances of 3.8399 (3) and 4.7530 (2) Å. The observed P—Se distances and Se—P—Se angles agree with other salts of this anion.

Related literature

For similar selenophosphate compounds, see: Biswas *et al.* (2010); Lin *et al.* (2012). For ionothermal reactions in room-temperature ionic liquids, see: Morris (2009); Parnham & Morris (2007); Cody *et al.* (2012). For the preparation of EMIM(BF_4), see: Egashira *et al.* (2006). For the structure of the $P_2Se_8^{2-}$ anion, see: Zhao *et al.* (1992); Rotter *et al.* (2008). For π–π interactions between imidazolium cations, see: Wilkes & Zaworotko (1993).



Experimental

Crystal data

$2C_6H_{11}N_2^+\cdot P_2Se_8^{2-}$
M_r = 915.96
Triclinic, $P\bar{1}$
a = 7.8885 (4) Å
b = 9.3783 (4) Å
c = 9.8039 (5) Å
α = 110.390 (3)°
β = 96.395 (4)°
γ = 102.992 (5)°
V = 648.00 (5) Å^3
Z = 1
Mo *K*α radiation
μ = 11.41 mm^{-1}
T = 293 K
0.19 × 0.07 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: Gaussian [*JANA2006* (Petříček *et al.*, 2006) and *X-SHAPE* (Stoe & Cie, 1998)]
T_{min} = 0.204, T_{max} = 0.754
22118 measured reflections
3719 independent reflections
2622 reflections with $I > 2\sigma(I)$
R_{int} = 0.072

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.063
S = 1.02
3719 reflections
118 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—Se4	2.1104 (8)	P1—Se2^i	2.2809 (8)
P1—Se3	2.1334 (8)	Se1—Se2	2.3442 (5)
P1—Se1	2.2794 (9)		
Se4—P1—Se3	122.19 (4)	Se3—P1—Se2^i	100.49 (3)
Se4—P1—Se1	113.49 (4)	Se1—P1—Se2^i	104.32 (3)
Se3—P1—Se1	100.04 (3)	P1—Se1—Se2	102.89 (2)
Se4—P1—Se2^i	113.90 (4)	P1^i—Se2—Se1	102.37 (2)

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

Data collection: *COLLECT* (Hooft, 2009); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2012); 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: NC2314).

References

Biswas, K., Zhang, Q., Chung, I., Song, J., Androulakis, J., Freeman, A. J. & Kanatzidis, M. G. (2010). *J. Am. Chem. Soc.* **132**, 14760–14762.
Brandenburg, K. & Putz, H. (2012). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Cody, J. A., Finch, K. B., Reynders, G. J. III, Alexander, G. C. B., Lim, H. G., Näther, C. & Bensch, W. (2012). *Inorg. Chem.* **51**, 13357–13362.
Egashira, M., Yamamoto, Y., Fukutake, T., Yoshimoto, N. & Morita, M. (2006). *J. Fluorine Chem.* **127**, 1261–1264.
Hooft, R. W. W. (2009). *COLLECT*. Nonius BV, Delft, The Netherlands.
Lin, Y., Massa, W. & Dehnen, S. (2012). *Chem. Eur. J.* **18**, 13427–, 13434.
Morris, R. E. (2009). *Chem. Commun.* pp. 2990–2998.
Parnham, E. R. & Morris, R. E. (2007). *Acc. Chem. Res.* **40**, 1005–1013.

Petříček, V., Dušek, M. & Palatinus, L. (2006). *JANA2006*. Institute of Physics, Praha, Czech Republic.
Rotter, C., Schuster, M., Kidik, M., Schön, O., Klapötke, T. M. & Karaghiosoff, K. (2008). *Inorg. Chem.* **47**, 1663–1673.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Stoe & Cie (1998). *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Wilkes, J. S. & Zaworotko, M. J. (1993). *Supramol. Chem.* **1**, 191–193.
Zhao, J., Pennington, W. T. & Kolis, J. W. (1992). *J. Chem. Soc. Chem. Commun.* pp. 265–266.

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Bis(1-ethyl-3-methylimidazolium) 3,6-diselanylidene-1,2,4,5-tetraselena-3,6-diphosphacyclohexane-3,6-diselenolate

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S1. Comment

Thiophosphate and selenophosphate compounds are sought for their interesting and fine-tunable electronic properties (Lin *et al.*, 2012). As new synthetic methods are often needed to gain access to new compounds with interesting properties, ionothermal reactions of thio- and selenophosphates were explored. Recently, room-temperature ionic liquids have received much interest for the preparation of inorganic materials (Morris, 2009; Parnham & Morris, 2007; Cody, *et al.*, 2012).

The structure of the anion in the title compound was first reported by Zhao *et al.* (1992) and the EMIM cation is well known. All interatomic distances and angles found in the current study (Fig. 1) are within normal ranges (Rotter *et al.*, 2008). Although the EMIM cations are found in columns in the title compound, the centroid-to-centroid distances of 3.8399 (3) Å and 4.7530 (2) Å (Fig. 2) indicate only weak pi-pi interactions (Wilkes & Zaworotko, 1993).

S2. Experimental

The title compound was prepared by the literature method (Cody *et al.*, 2012) for ionothermal synthesis of related sulfur compounds. A total mass of 125 mg of the elements with a stoichiometry of Ni: 4P: 16Se was ground together in a glove box and then placed in a Pyrex tube. An aliquot of 1.25 ml of the ionic liquid EMIMBF$_4$, prepared according to the literature (Egashira, *et al.*, 2006), was added to the tube in a glove bag. The tube was then evacuated and sealed. The reaction mixture was heated at 150 °C for 96 h and then slowly cooled to room temperature at a rate of 0.5 °C/min. The tube was opened, the product mixture was filtered, and individual crystals were selected for analysis by hand. The products included black powder, large red blocks, and small yellow plates. The latter were both the title compound; the color difference is attributed to absorption effects from the thickness of the crystals. Although elemental nickel was included in the reaction mixture, it was not observed in the isolated crystalline products.

S3. Refinement

All H atoms were positioned with idealized geometry and were refined isotropically with U_{iso}(H) = 1.2 U_{eq}(C) (1.5 for methyl H atoms) using a riding model with C—H = 0.93 Å for aromatic, 0.97 Å for methylene and 0.96 Å for methyl H-atoms.

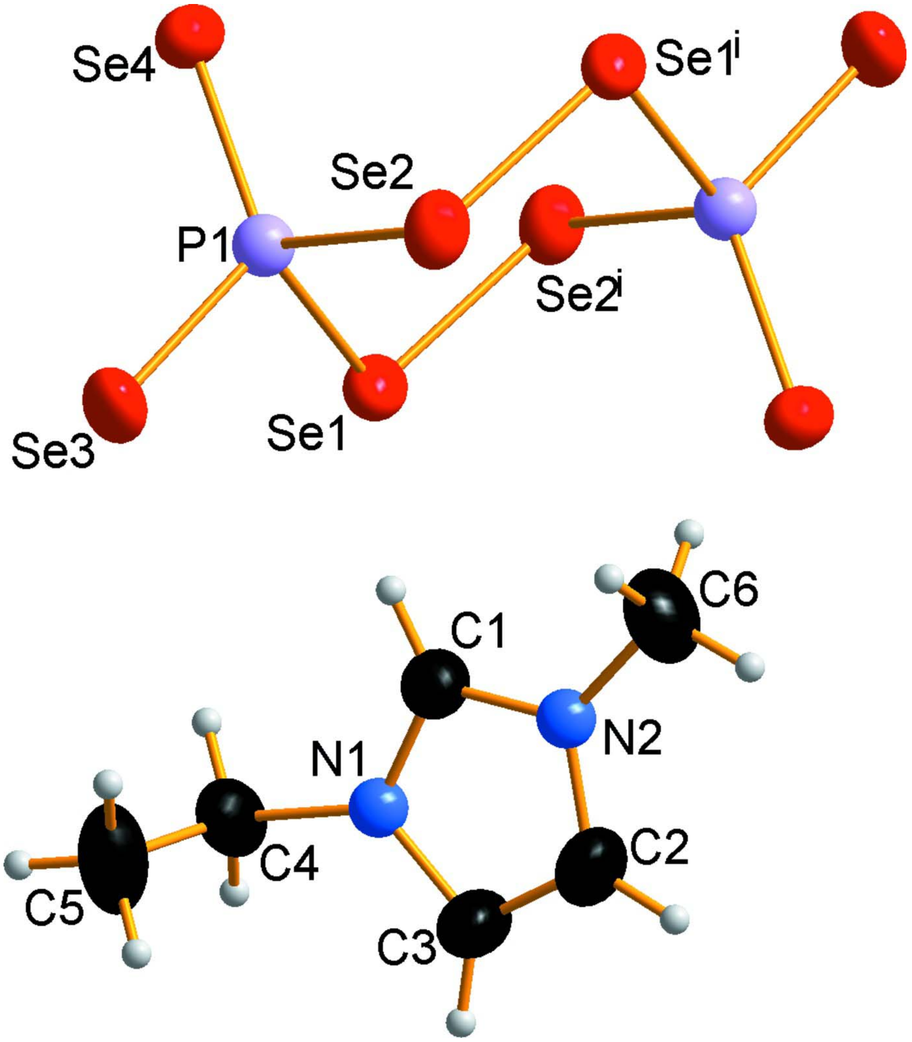

Figure 1

Molecular structure and atomic labeling scheme for the title compound. Thermal elipsoids are shown at the 50% level. Symmetry code for the generation of equivalent atoms: i = 1 - *x*, -*y*, -*z*.

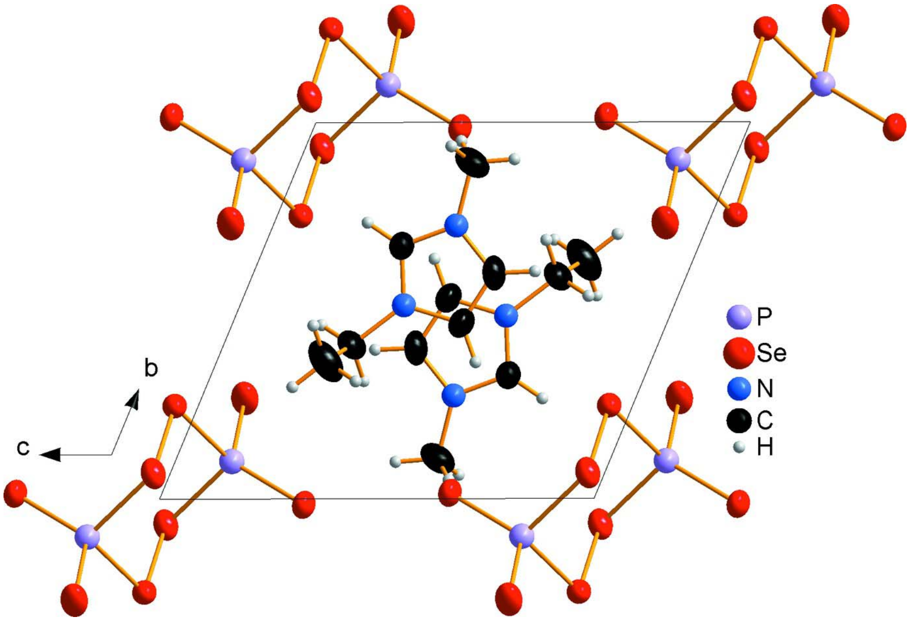

Figure 2

A packing diagram of the title compound showing the column of EMIM cations along the *a* axis.

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$c = 9.8039$ (5) Å
$\alpha = 110.390$ (3)°
$\beta = 96.395$ (4)°
$\gamma = 102.992$ (5)°
$V = 648.00$ (5) Å^3

$Z = 1$
$F(000) = 424$
$D_x = 2.347$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3719 reflections
$\theta = 6.5$–30.0°
$\mu = 11.41$ mm^{-1}
$T = 293$ K
Plate, yellow
0.19 × 0.07 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Unknown monochromator
ω scans
Absorption correction: gaussian [JANA2006 (Petříček *et al.*, 2006) and *X-SHAPE* (Stoe & Cie, 1998)]
$T_{\min} = 0.204$, $T_{\max} = 0.754$

22118 measured reflections
3719 independent reflections
2622 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$
$\theta_{\max} = 30.0°$, $\theta_{\min} = 6.5°$
$h = -10 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.063$
$S = 1.02$
3719 reflections
118 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2 + 0.2292P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

Special details

Experimental. A set of 280 frames were collected with a rotation of 2° per frame and an exposure time of 190 s; the crystal to detector distance was 25.00 mm. Refinements were done with the *SHELXTL97* (Sheldrick, 2008) software package; absorption correction was made with the program Jana2006 (Petricek *et al.*, 2006) using the program *X-SHAPE* (Stoe & Cie, 1998).

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.62769 (11)	−0.10004 (9)	0.13027 (9)	0.03455 (17)
Se1	0.38273 (4)	−0.24755 (3)	−0.05425 (4)	0.04208 (9)
Se2	0.21381 (4)	−0.06847 (4)	−0.03916 (4)	0.04234 (9)
Se3	0.77764 (6)	−0.26777 (5)	0.09996 (4)	0.05519 (11)
Se4	0.56642 (5)	0.01558 (4)	0.33743 (4)	0.04503 (10)
N1	0.2827 (4)	0.4858 (3)	0.3773 (3)	0.0413 (6)
N2	0.2005 (3)	0.2740 (3)	0.4218 (3)	0.0422 (6)
C1	0.2281 (4)	0.3279 (4)	0.3154 (4)	0.0415 (7)
H1	0.2122	0.2661	0.2148	0.050*
C2	0.2379 (5)	0.4007 (5)	0.5542 (4)	0.0530 (9)
H2	0.2298	0.3961	0.6465	0.064*
C3	0.2884 (5)	0.5333 (4)	0.5270 (4)	0.0525 (9)
H3	0.3210	0.6372	0.5965	0.063*
C4	0.3182 (5)	0.5911 (4)	0.2952 (4)	0.0486 (8)
H4A	0.3597	0.5382	0.2068	0.058*
H4B	0.4115	0.6869	0.3572	0.058*
C5	0.1558 (6)	0.6340 (6)	0.2513 (6)	0.0735 (13)
H5A	0.1832	0.7026	0.1986	0.110*
H5B	0.1156	0.6877	0.3388	0.110*
H5C	0.0641	0.5395	0.1883	0.110*
C6	0.1325 (5)	0.1069 (4)	0.3983 (5)	0.0606 (10)

H6A	0.1248	0.0980	0.4922	0.091*
H6B	0.2114	0.0496	0.3527	0.091*
H6C	0.0165	0.0634	0.3345	0.091*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0454 (4)	0.0353 (4)	0.0258 (4)	0.0132 (3)	0.0065 (3)	0.0144 (3)
Se1	0.0560 (2)	0.03274 (15)	0.03188 (17)	0.00568 (13)	0.00294 (14)	0.01201 (13)
Se2	0.03936 (17)	0.05217 (19)	0.03963 (19)	0.00924 (13)	0.00866 (14)	0.02474 (16)
Se3	0.0774 (3)	0.0598 (2)	0.0454 (2)	0.0411 (2)	0.01621 (19)	0.02586 (19)
Se4	0.0639 (2)	0.04233 (17)	0.02882 (17)	0.01506 (15)	0.01340 (15)	0.01247 (14)
N1	0.0472 (15)	0.0410 (14)	0.0361 (15)	0.0097 (11)	0.0087 (12)	0.0172 (12)
N2	0.0435 (14)	0.0439 (15)	0.0431 (16)	0.0089 (11)	0.0079 (12)	0.0239 (13)
C1	0.0461 (18)	0.0424 (16)	0.0338 (17)	0.0084 (13)	0.0078 (14)	0.0147 (14)
C2	0.063 (2)	0.066 (2)	0.036 (2)	0.0179 (18)	0.0138 (17)	0.0268 (19)
C3	0.071 (2)	0.0468 (18)	0.0329 (18)	0.0121 (17)	0.0126 (17)	0.0101 (16)
C4	0.054 (2)	0.0459 (18)	0.052 (2)	0.0092 (15)	0.0174 (17)	0.0277 (17)
C5	0.065 (3)	0.095 (3)	0.095 (4)	0.030 (2)	0.025 (2)	0.069 (3)
C6	0.064 (2)	0.051 (2)	0.075 (3)	0.0095 (17)	0.013 (2)	0.038 (2)

Geometric parameters (Å, º)

P1—Se4	2.1104 (8)	C2—C3	1.345 (5)
P1—Se3	2.1334 (8)	C2—H2	0.9300
P1—Se1	2.2794 (9)	C3—H3	0.9300
P1—Se2^{i}	2.2809 (8)	C4—C5	1.489 (5)
Se1—Se2	2.3442 (5)	C4—H4A	0.9700
Se2—P1^{i}	2.2809 (8)	C4—H4B	0.9700
N1—C1	1.332 (4)	C5—H5A	0.9600
N1—C3	1.370 (4)	C5—H5B	0.9600
N1—C4	1.477 (4)	C5—H5C	0.9600
N2—C1	1.327 (4)	C6—H6A	0.9600
N2—C2	1.366 (4)	C6—H6B	0.9600
N2—C6	1.463 (4)	C6—H6C	0.9600
C1—H1	0.9300		

Se4—P1—Se3	122.19 (4)	C2—C3—H3	126.6
Se4—P1—Se1	113.49 (4)	N1—C3—H3	126.6
Se3—P1—Se1	100.04 (3)	N1—C4—C5	111.4 (3)
Se4—P1—Se2^{i}	113.90 (4)	N1—C4—H4A	109.3
Se3—P1—Se2^{i}	100.49 (3)	C5—C4—H4A	109.3
Se1—P1—Se2^{i}	104.32 (3)	N1—C4—H4B	109.3
P1—Se1—Se2	102.89 (2)	C5—C4—H4B	109.3
P1^{i}—Se2—Se1	102.37 (2)	H4A—C4—H4B	108.0
C1—N1—C3	108.8 (3)	C4—C5—H5A	109.5
C1—N1—C4	125.1 (3)	C4—C5—H5B	109.5
C3—N1—C4	126.0 (3)	H5A—C5—H5B	109.5

C1—N2—C2	108.5 (3)	C4—C5—H5C	109.5
C1—N2—C6	125.1 (3)	H5A—C5—H5C	109.5
C2—N2—C6	126.3 (3)	H5B—C5—H5C	109.5
N2—C1—N1	108.3 (3)	N2—C6—H6A	109.5
N2—C1—H1	125.9	N2—C6—H6B	109.5
N1—C1—H1	125.9	H6A—C6—H6B	109.5
C3—C2—N2	107.8 (3)	N2—C6—H6C	109.5
C3—C2—H2	126.1	H6A—C6—H6C	109.5
N2—C2—H2	126.1	H6B—C6—H6C	109.5
C2—C3—N1	106.7 (3)		

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