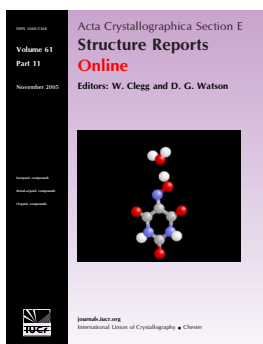


Ammonium *O,O'*-diethyl dithiophosphate

Andrzej Okuniewski and Barbara Becker

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Ammonium *O,O'*-diethyl dithiophosphate

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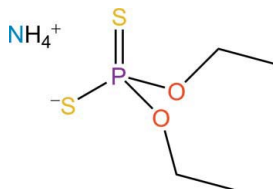
Received 10 June 2011; accepted 13 June 2011

Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.035; wR factor = 0.085; data-to-parameter ratio = 18.4.

In the title compound, $\text{NH}_4^+(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$, the ammonium cation is connected by four charge-assisted $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds to four tetrahedral *O,O'*-diethyl dithiophosphate anions, forming layers parallel to (100). The polar and non-polar constituents of the layers are stacked alternately along [100]. Interlacing of the external ethyl groups through van der Waals interactions combines these layers into a three-dimensional structure.

Related literature

For related structures, see: Chekhlov *et al.* (1991); Chekhlov (2000). For applications of *O,O'*-diethyl dithiophosphate in coordination chemistry, see: Cotero-Villegas *et al.* (2011). For the determination of various ions in analytical chemistry using *O,O'*-diethyl dithiophosphates, see: Carletto *et al.* (2009); Maltez *et al.* (2008); Pozebon *et al.* (1998); Wu *et al.* (2006). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

$\text{NH}_4^+\cdot\text{C}_4\text{H}_{10}\text{O}_2\text{PS}_2^-$
 $M_r = 203.25$
Monoclinic, $P2_1/c$
 $a = 12.0274$ (7) Å
 $b = 7.2006$ (3) Å
 $c = 12.5690$ (7) Å
 $\beta = 110.305$ (6)°

$V = 1020.89$ (9) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.63$ mm⁻¹
 $T = 120$ K
 $0.30 \times 0.16 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer
Absorption correction: analytical [*CrysAlis PRO* (Oxford Diffraction, 2010) using a multi-faceted crystal model based on expressions derived by Clark &

Reid (1995)]
 $T_{\min} = 0.856$, $T_{\max} = 0.969$
3955 measured reflections
2004 independent reflections
1579 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.085$
 $S = 1.01$
2004 reflections
109 parameters
4 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.46$ e Å⁻³
 $\Delta\rho_{\min} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{S1}^{\text{i}}$	0.89 (1)	2.43 (1)	3.310 (2)	178 (3)
$\text{N1}-\text{H4N}\cdots\text{S1}^{\text{ii}}$	0.88 (1)	2.50 (1)	3.377 (2)	177 (2)
$\text{N1}-\text{H3N}\cdots\text{S2}^{\text{iii}}$	0.89 (1)	2.54 (1)	3.409 (2)	169 (2)
$\text{N1}-\text{H2N}\cdots\text{S2}$	0.88 (1)	2.39 (1)	3.2633 (19)	171 (2)

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2499).

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supplementary materials

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Ammonium *O,O'*-diethyl dithiophosphate

A. Okuniewski and B. Becker

Comment

Ammonium *O,O'*-diethyl dithiophosphate is frequently used as a source of the $(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$ ligand in coordination chemistry (Cotero-Villegas *et al.*, 2011) and in analytical chemistry for determination of various ions, *eg.* As (Pozebon *et al.*, 1998), Pb (Maltez *et al.*, 2008), Cd (Carletto *et al.*, 2009), Hg (Wu *et al.*, 2006).

There are at least 340 structures deposited in the Cambridge Structural Database (v5.32; Allen, 2008) containing the *O,O'*-diethyl dithiophosphate moiety, but there are no crystal structure of simple ammonium, sodium or potassium salts reported. Among these structures one can find 328 complexes (including 204 of row 6 family metals, mainly molybdenum compounds), five compounds with complex cations, five simple organic or inorganic compounds and finally two salts of 1,10-diaza-18-crown-6 (Chekhlov, 2000; Chekhlov *et al.*, 1991).

In the crystal structure of the title compound, the asymmetric unit consists of one ammonium cation and one tetrahedral *O,O'*-diethyl dithiophosphate anion (Fig. 1). The P—S distances are 1.9720 (8) Å and 1.9753 (8) Å. These values are slightly lower than the mean value of 1.9872 (25) Å calculated for the 340 compounds deposited in the CSD. Each ammonium cation is connected by four N—H··S hydrogen bonds to four *O,O'*-diethyl dithiophosphate anions. This way three structural ring motifs are formed: two of them are centrosymmetric – $\text{R}^2_4(8)$, $\text{R}^4_4(12)$, and one is not – $\text{R}^3_4(10)$ (Fig. 2.) Hydrogen bonding interactions are summarized in Tab. 1.

The connected ions form layers parallel to the (100) plane. Each layer has an hydrophilic interior, where heteroatoms and hydrogen bonds can be found, and an hydrophobic exterior formed by the ethyl groups (Fig. 3). These layers interact with each other by van der Waals forces forming a three-dimensional crystal structure.

Experimental

1 g of commercially available ammonium *O,O'*-diethyl dithiophosphate was dissolved in 5 ml of acetone and left to evaporate slowly. After one week colourless crystals suitable for single-crystal X-ray diffraction analysis were collected.

Refinement

Hydrogen atoms were placed at the calculated positions ($d_{\text{CH}} = 0.98\text{--}0.99$ Å) and were treated as riding on their parent atoms, with $U(\text{H})$ set to 1.2–1.5 times $U_{\text{eq}}(\text{C})$. The N—H distances were restrained to 0.88 (1) Å.

Figures

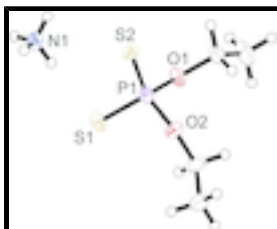


Fig. 1. The molecular structure of $\text{NH}_4^+(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$, with displacement ellipsoids drawn at the 50% probability level.



Fig. 2. Hydrogen bond pattern found in the structure of $\text{NH}_4^+(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$, with $\mathbf{R}^2_4(8)$, $\mathbf{R}^4_4(12)$ and $\mathbf{R}^3_4(10)$ structural motifs depicted. Hydrogen bonds are marked with dashed lines.

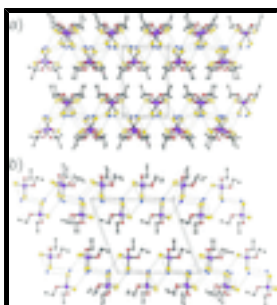
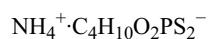


Fig. 3. Layers of $\text{NH}_4^+(\text{C}_2\text{H}_5\text{O})_2\text{PS}_2^-$ projected down $[001]$ (a) and $[010]$ (b). Hydrogen bonds are marked with dashed lines, with hydrogen atoms omitted for clarity.

Ammonium *O,O'*-diethyl dithiophosphate

Crystal data



$$M_r = 203.25$$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$$a = 12.0274\ (7)\ \text{\AA}$$

$$b = 7.2006\ (3)\ \text{\AA}$$

$$c = 12.5690\ (7)\ \text{\AA}$$

$$\beta = 110.305\ (6)^\circ$$

$$V = 1020.89\ (9)\ \text{\AA}^3$$

$$Z = 4$$

$$F(000) = 432$$

$$D_x = 1.322\ \text{Mg m}^{-3}$$

Melting point: 438(1) K

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2402 reflections

$$\theta = 2.8\text{--}28.4^\circ$$

$$\mu = 0.63\ \text{mm}^{-1}$$

$$T = 120\ \text{K}$$

Plate, colourless

$$0.30 \times 0.16 \times 0.05\ \text{mm}$$

Data collection

Oxford Diffraction Xcalibur
diffractometer

graphite

Detector resolution: 8.1883 pixels mm^{-1}

ω scans

Absorption correction: analytical

2004 independent reflections

1579 reflections with $I > 2\sigma(I)$

$$R_{\text{int}} = 0.023$$

$$\theta_{\text{max}} = 26.0^\circ, \theta_{\text{min}} = 3.3^\circ$$

$$h = -14 \rightarrow 12$$

[*CrysAlis PRO* (Oxford Diffraction, 2010) using a multi-faceted crystal model based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.856$, $T_{\max} = 0.969$

$k = -8 \rightarrow 8$

3955 measured reflections

$l = -15 \rightarrow 14$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.035$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.085$

H atoms treated by a mixture of independent and constrained refinement

$S = 1.01$

$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2]$

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

2004 reflections

$(\Delta/\sigma)_{\max} = 0.001$

109 parameters

$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$

4 restraints

$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Special details

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3199 (2)	0.5211 (3)	0.2964 (2)	0.0326 (5)
H1A	0.2982	0.4906	0.3635	0.039*
H1B	0.265	0.6179	0.2517	0.039*
C2	0.4451 (2)	0.5890 (4)	0.3330 (3)	0.0511 (7)
H2A	0.4984	0.493	0.3783	0.077*
H2B	0.4529	0.7018	0.3788	0.077*
H2C	0.466	0.6169	0.266	0.077*
C3	0.3169 (2)	0.0606 (4)	0.3984 (2)	0.0392 (6)
H3A	0.369	0.1581	0.4457	0.047*
H3B	0.36	-0.0022	0.3543	0.047*
C4	0.2849 (3)	-0.0763 (4)	0.4717 (2)	0.0425 (7)
H4A	0.2426	-0.0129	0.5152	0.064*
H4B	0.3572	-0.1334	0.524	0.064*

supplementary materials

H4C	0.234	-0.1727	0.4242	0.064*
O1	0.31244 (13)	0.35602 (19)	0.22740 (13)	0.0281 (4)
O2	0.20831 (13)	0.1435 (2)	0.32198 (12)	0.0278 (4)
P1	0.20257 (5)	0.21895 (8)	0.20040 (5)	0.02272 (16)
S1	0.23286 (5)	0.02043 (8)	0.10585 (5)	0.03012 (17)
S2	0.04716 (5)	0.34439 (8)	0.13990 (4)	0.02542 (16)
N1	0.0076 (2)	0.3099 (3)	0.38320 (17)	0.0284 (4)
H1N	-0.0563 (17)	0.369 (4)	0.385 (2)	0.053 (8)*
H2N	0.020 (2)	0.333 (4)	0.3191 (14)	0.047 (8)*
H3N	-0.010 (3)	0.1909 (16)	0.385 (2)	0.052 (9)*
H4N	0.0644 (18)	0.357 (3)	0.4414 (15)	0.047 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0318 (13)	0.0262 (11)	0.0376 (13)	-0.0028 (10)	0.0093 (10)	-0.0092 (10)
C2	0.0360 (15)	0.0437 (15)	0.0672 (19)	-0.0085 (13)	0.0101 (14)	-0.0231 (15)
C3	0.0281 (13)	0.0406 (14)	0.0387 (14)	0.0043 (12)	-0.0015 (11)	0.0107 (12)
C4	0.0528 (17)	0.0459 (15)	0.0302 (13)	0.0196 (14)	0.0162 (12)	0.0099 (12)
O1	0.0263 (8)	0.0254 (8)	0.0348 (8)	-0.0061 (7)	0.0133 (7)	-0.0074 (7)
O2	0.0250 (8)	0.0333 (8)	0.0231 (7)	0.0047 (7)	0.0061 (6)	0.0067 (7)
P1	0.0227 (3)	0.0229 (3)	0.0233 (3)	-0.0008 (2)	0.0088 (2)	-0.0015 (2)
S1	0.0256 (3)	0.0295 (3)	0.0370 (3)	-0.0010 (2)	0.0131 (3)	-0.0097 (3)
S2	0.0263 (3)	0.0297 (3)	0.0202 (3)	0.0051 (2)	0.0080 (2)	0.0011 (2)
N1	0.0328 (12)	0.0313 (12)	0.0244 (10)	0.0047 (10)	0.0141 (9)	0.0026 (9)

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

C1—O1	1.456 (3)	C4—H4A	0.98
C1—C2	1.495 (3)	C4—H4B	0.98
C1—H1A	0.99	C4—H4C	0.98
C1—H1B	0.99	O1—P1	1.5888 (15)
C2—H2A	0.98	O2—P1	1.6005 (14)
C2—H2B	0.98	P1—S1	1.9720 (8)
C2—H2C	0.98	P1—S2	1.9753 (8)
C3—O2	1.454 (3)	N1—H1N	0.886 (10)
C3—C4	1.489 (3)	N1—H2N	0.884 (10)
C3—H3A	0.99	N1—H3N	0.885 (10)
C3—H3B	0.99	N1—H4N	0.879 (10)
O1—C1—C2	107.3 (2)	C3—C4—H4B	109.5
O1—C1—H1A	110.2	H4A—C4—H4B	109.5
C2—C1—H1A	110.2	C3—C4—H4C	109.5
O1—C1—H1B	110.2	H4A—C4—H4C	109.5
C2—C1—H1B	110.2	H4B—C4—H4C	109.5
H1A—C1—H1B	108.5	C1—O1—P1	120.63 (14)
C1—C2—H2A	109.5	C3—O2—P1	120.07 (15)
C1—C2—H2B	109.5	O1—P1—O2	104.47 (8)
H2A—C2—H2B	109.5	O1—P1—S1	105.37 (6)

C1—C2—H2C	109.5	O2—P1—S1	111.94 (6)
H2A—C2—H2C	109.5	O1—P1—S2	113.83 (6)
H2B—C2—H2C	109.5	O2—P1—S2	104.14 (6)
O2—C3—C4	108.3 (2)	S1—P1—S2	116.59 (4)
O2—C3—H3A	110	H1N—N1—H2N	111 (2)
C4—C3—H3A	110	H1N—N1—H3N	104 (3)
O2—C3—H3B	110	H2N—N1—H3N	109 (2)
C4—C3—H3B	110	H1N—N1—H4N	103 (2)
H3A—C3—H3B	108.4	H2N—N1—H4N	111 (3)
C3—C4—H4A	109.5	H3N—N1—H4N	118 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H1N···S1 ⁱ	0.89 (1)	2.43 (1)	3.310 (2)	178 (3)
N1—H4N···S1 ⁱⁱ	0.88 (1)	2.50 (1)	3.377 (2)	177 (2)
N1—H3N···S2 ⁱⁱⁱ	0.89 (1)	2.54 (1)	3.409 (2)	169 (2)
N1—H2N···S2	0.88 (1)	2.39 (1)	3.2633 (19)	171 (2)

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

Fig. 1

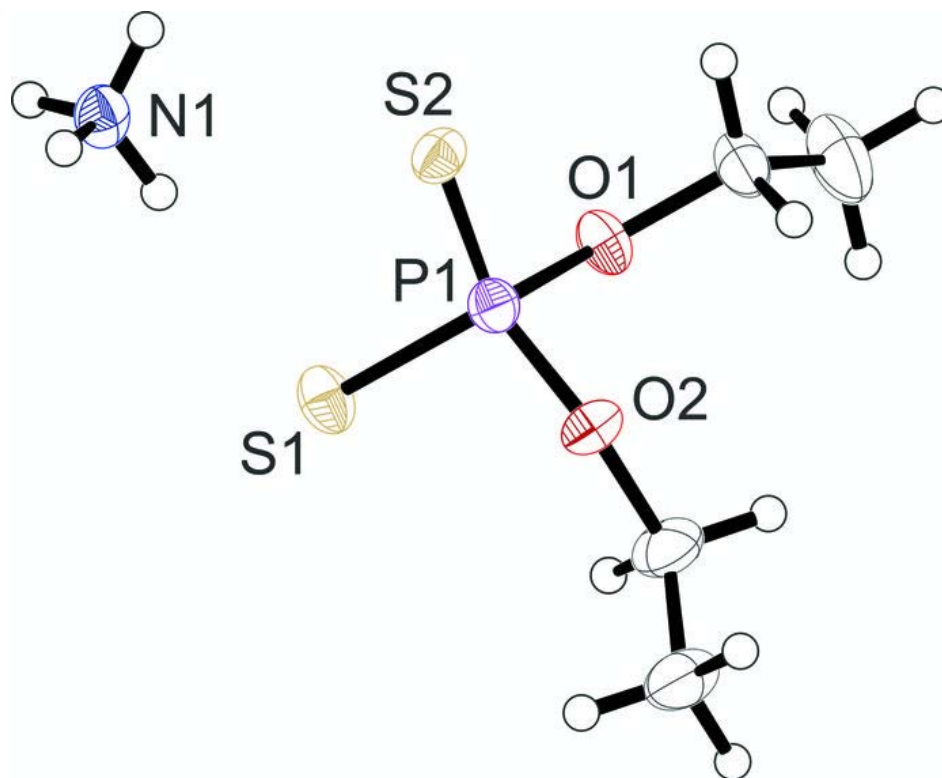


Fig. 2

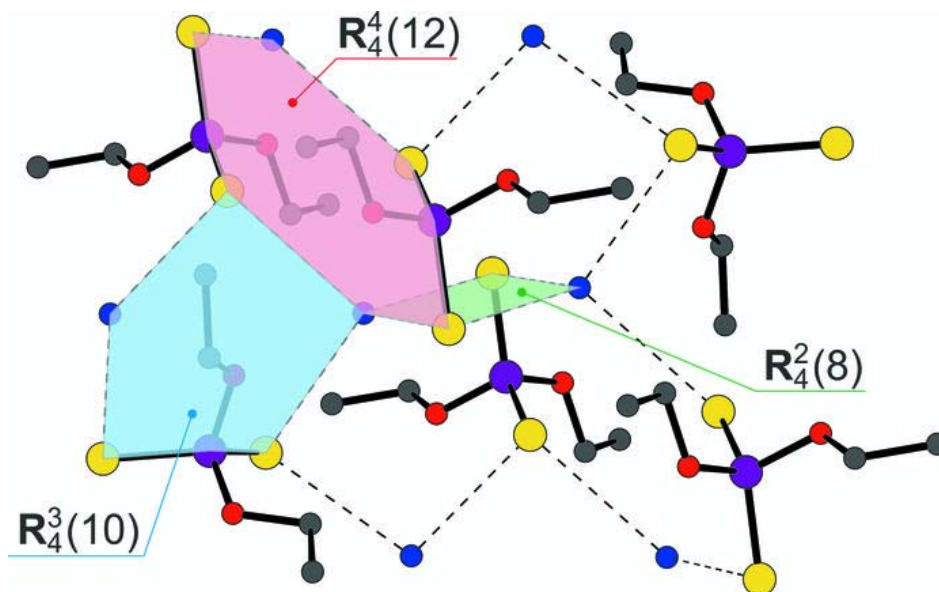


Fig. 3

