organic compounds

Ammonium O,O-dicyclohexyl phosphorodithioate

Mustafa Serkan Soylu,ª* Mehtap Yağan,ᵇ Nezihe Çalışkan,ᶜ Bekir Batıᵇ and Orhan Büyükgüngörᶜ

ªDepartment of Physics, Giresun Faculty of Arts and Sciences, Karadeniz Technical University, 28100 Giresun, Turkey, ᵇDepartment of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey, and ᶜDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

Correspondence e-mail: mssoylu@omu.edu.tr

The structure of the title compound, $NH_4^+ \cdot C_{12}H_{22}O_2PS_2^-$, consists of a polymeric arrangement of ammonium cations and O,O-dicyclohexyl phosphorodithioate anions linked through N—H···O and N—H···S hydrogen bonds. These interactions result in the formation of (100) sheets.

Comment

Organodithio derivatives of phosphorus have been widely studied for many years (Larson, 2004; Gray *et al.*, 2004; Ivanov *et al.*, 2000). The corresponding acids and metal complexes of phosphorodithioates (Dtph) have been shown to have many industrial and agricultural applications (Gray *et al.*, 2003, 2004). For example, coordination compounds of transition metals with these ligands are used in agriculture as fungicides. They also function as antioxidants and corrosion inhibitors (Ivanov *et al.*, 2000). Sodium or potassium salts of O,O′-dialkyl phosphorodithioates are used as selective collector reagents of sulfide minerals (Gray *et al.*, 2003, 2004; Ivanov *et al.*, 2000; Larson, 2004). These complexes can be mono-, di- or poly-nuclear, the choice being mainly determined by the ability of the Dtph ligands to perform terminal, bridging or mixed

$R_1 = p$-methoxyphenyl

$R_2 = $ methyl in (IIIa) and isopropyl in (IIIb)
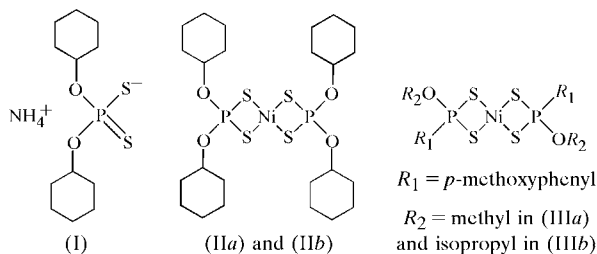
structural functions (El-Khaldy *et al.*, 2003). Nickel complexes of Dtph ligands are mononuclear, while zinc complexes of the ligands are dinuclear (Gray *et al.*, 2003, 2004; Ivanov *et al.*, 2000).

The crystal structure determination of the title compound, (I) (Fig. 1), was carried out in order to determine the strength of the hydrogen-bond capability between the molecules of the Dtph ligands, and also to establish the local symmetry around the P atom.

The asymmetric unit of (I) contains one cation and one anion. The coordination around the P atom is distorted tetrahedral. Selected bond distances and angles of (I) are compared in Table 1 with those of some previously reported nickel complexes of (I) and (II) (Lin *et al.*, 1987; Taş *et al.*, 2005), and two nickel complexes of related dialkyl phosphorodithioate ligands, (IIIa) and (IIIb) (Gray *et al.*, 2003, 2004). While the P—S bond lengths of (I) are shorter than the corresponding values reported for nickel complexes of (II), (IIIa) and (IIIb), the O—P distances are longer.

The ions in (I) are linked *via* N—H···O and N—H···S hydrogen bonds (Table 2). Within the selected asymmetric
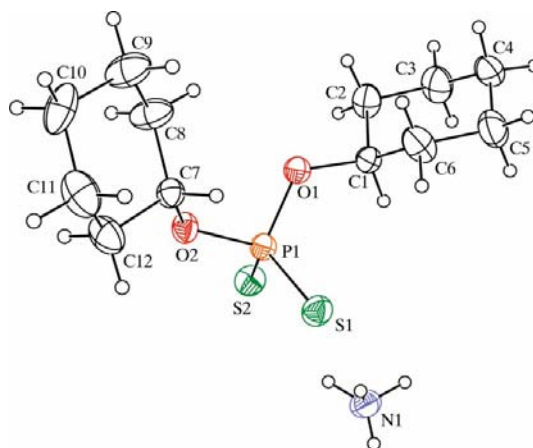

Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.
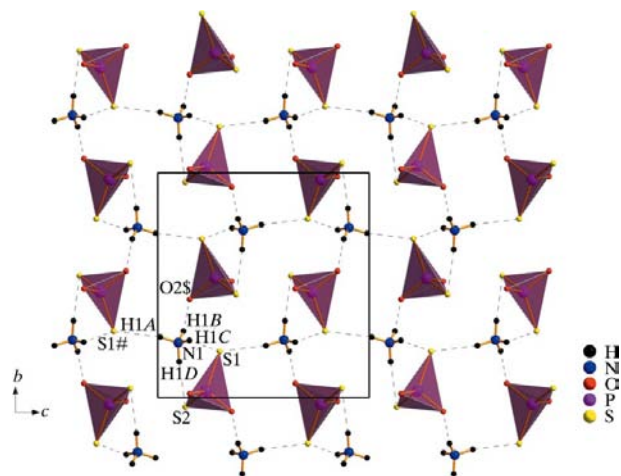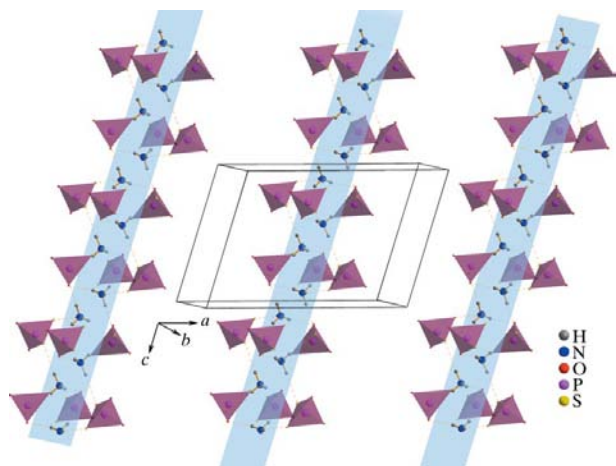

Figure 2
Hydrogen-bond (dashed lines) and polyhedral representation of (I), in a view along the (100) axis. Distorted PS_2O_2 tetrahedra are shaded dark and cyclohexyl groups have been omitted for clarity. Atoms labelled with a hash (#) or dollar sign ($) are at the symmetry positions $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

organic compounds

Figure 3
A view of how the propagation by translation and inversion of all hydrogen-bond interactions (dashed lines) linking pseudo-tetrahedra generates (200) sheets. The distance between these sheets is 14.406 Å.

unit, atoms H1*A* and H1*B* of the cation act as hydrogen-bond donors to atoms S1 and S2 of the anion. In addition, atoms H1*C* and H1*D* at (x, y, z) act as donors to atoms S1 and O2 at $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively (Table 2). These interactions generate $R_8^6(20)$ and $R_2^2(6)$ rings (Bernstein *et al.*, 1995) (Fig. 2). Propagation by translation and inversion of all these rings linking pseudo-tetrahedra then generates (100) sheets (Figs. 2 and 3). The distance between these sheets is 14.406 Å.

Experimental

The title compound was prepared based on a literature procedure (Ma *et al.*, 1995). Phosphorus pentasulfide (0.25 mol, 27.8 g; Acros Organics) and benzene (60 ml) were heated in a water bath at 348–353 K. Cyclohexanol (1 mol, 55 ml; Merck) was added dropwise with stirring and condensing under a nitrogen atmosphere. After refluxing for 3 h with stirring, ammonia gas was bubbled through the hot solution until the gas started to appear from the condenser, during which a white precipitate appeared. The solution was cooled slowly to room temperature. The product was filtered off, rinsed three times with 20 ml of benzene and dried under reduced pressure (yield *ca* 50%).

Crystal data

$NH_4^+ \cdot C_{12}H_{22}O_2PS_2^-$	$D_x = 1.275$ Mg m^{-3}
$M_r = 311.43$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 18994
$a = 15.0755$ (11) Å	reflections
$b = 10.6965$ (5) Å	$\theta = 1.9$–$27.6°$
$c = 10.5305$ (7) Å	$\mu = 0.42$ mm^{-1}
$\beta = 107.123$ (5)$°$	$T = 293$ (2) K
$V = 1622.83$ (18) Å^3	Irregular, colourless
$Z = 4$	$0.57 \times 0.37 \times 0.17$ mm

Data collection

Stoe IPDS-2 diffractometer	2862 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.038$
Absorption correction: integration	$\theta_{max} = 27.6°$
(X-$RED32$; Stoe & Cie, 2002)	$h = -19 \rightarrow 19$
$T_{min} = 0.832$, $T_{max} = 0.934$	$k = -13 \rightarrow 13$
18994 measured reflections	$l = -13 \rightarrow 13$
3723 independent reflections	

Table 1
Comparison of geometric parameters (Å, °) of (I) with those in the related compounds (II), (II*a*), (III*a*) and (III*b*).

Note that in (III*a*) and (III*b*), atom O1 is replaced by C1.

	(I)^a	(II)^b	(II*a*)^c	(III*a*)^d	(III*b*)^e
P1—S1	1.9794 (7)	1.9879 (8)	1.982 (4)	2.0043 (8)	2.0042 (8)
P1—S2	1.965787)	1.9917 (8)	1.992 (4)	2.0048 (7)	2.0082 (8)
P1—O1	1.5934 (14)	1.5566 (14)	1.565 (6)	1.7904 (18)	1.792 (2)
P1—O2	1.5974 (13)	1.5610 (14)	1.568 (7)	1.5856 (13)	1.5855 (15)
S1—P1—S2	117.01 (3)	101.74 (3)	101.75 (16)	102.77 (3)	101.80 (3)
O1—P1—S2	112.00 (5)	115.07 (7)	114.01 (3)	112.57 (7)	114.18 (8)
O2—P1—S1	111.49 (5)	115.34 (7)	115.4 (3)	113.59 (6)	114.90 (6)
O1—P1—O2	99.31 (7)	95.56 (7)	95.9 (3)	101.82 (7)	100.02 (9)

References: (*a*) this work; (*b*) Taş *et al.* (2005); (*c*) Lin *et al.* (1987); (*d*) Gray *et al.* (2003); (*e*) Gray *et al.* (2004).

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D \cdots A$	D—H$\cdots A$
N1—H1*A*$\cdots$S1^i	0.96 (4)	2.36 (4)	3.305 (2)	171 (3)
N1—H1*B*$\cdots$O2^{ii}	0.80 (4)	2.17 (4)	2.957 (3)	169 (3)
N1—H1*C*$\cdots$S1	0.80 (5)	2.56 (5)	3.318 (3)	159 (4)
N1—H1*D*$\cdots$S2	0.91 (6)	2.54 (6)	3.354 (2)	149 (4)

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$	$+ 0.213P]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
3723 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
179 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

H atoms of the ammonium cation were located in a difference map and refined isotropically. All other H atoms were treated as riding, with C—H distances of 0.97–0.98 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Brandenburg, K. (2005). *DIAMOND*. Demonstration Version 3.1. Crystal Impact GbR, Bonn, Germany.

El-Khaldy, A. A. S., Baraka, R. M. & El-Gomboz, R. A. A. (2003). *Synth. React. Inorg. Met. Org. Chem.* **33**, 195–204.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gray, I. P., Milton, H. L., Woollins, A. M. Z. & Woollins, J. D. (2003). *Dalton Trans.* pp. 3450–3457.
Gray, I. P., Slawin, A. M. Z. & Woollins, J. D. (2004). *Dalton Trans.* pp. 2477–2486.
Ivanov, A. V., Forsling, W., Kritikos, M., Anzutkin, O. N., Larson, A. C., Zhukov, F. A. & Yusupov, Z. F. (2000). *Dokl. Chem.* **1–3**, 236–241. (In Russian.)

Larson, A. C. (2004). PhD thesis, Luleå University of Technology, Sweden.
Lin, C., Liu, S., Xu, Z., Lin, J. & You, X. (1987). *Chin. J. Struct. Chem.* **6**, 186.
Ma, R., Mol, W. V. & Adams, F. (1995). *Anal. Chim. Acta*, **309**, 395–403.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
Taş, M., Yağan, M., Batı, H., Batı, B. & Büyükgüngör, O. (2005). *Acta Cryst.* E**61**, m1684–m1685.