with zero or negative intensity. Refinement on F^2 using all data was therefore impossible.

Data collection: *KM*4 *Software* (Kuma Diffraction, 1987) for (I) and (III); *XTL/XTLE* (Syntex, 1976) for (II). Cell refinement: *KM*4 *Software* for (I) and (III); *XTL/XTLE* for (II). Data reduction: *KM*4 *Software* for (I) and (III); *XTL/XTLE* for (II). For all compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1070). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Heinz, F. & Lamprecht, W. (1967). *Z. Physiol. Chem.* **348**, 855–863.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kuma Diffraction (1987). *Kuma KM4 User's Guide*. Version 3.1. Kuma Diffraction, Wrocław, Poland.

Lis, T. & Jerzykiewicz, L. (1996). *Acta Cryst.* C**52**, 129–134.

Lis, T. & Popek, T. (1993). *Pol. J. Chem.* **67**, 137–142.

Ott, E. & Krämer, K. (1933). *J. Prakt. Chem.* **137**, 255–256.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California, USA.

Taga, T., Ohashi, M. & Osaki, K. (1978). *Bull. Chem. Soc. Jpn*, **51**, 1697–1700.

Acta Cryst. (1996). C**52**, 2720-2724

Acid Salts of Phosphoenolpyruvic Acid (H_3PEP): $NaH_5(PEP)_2.2H_2O$ and $KH_5(PEP)_2$

TADEUSZ LIS

Department of Chemistry, University of Wrocław, ul. Joliot-Curie 14, 50-383 Wrocław, Poland. E-mail: tlis@ichuwr.chem.uni.wroc.pl

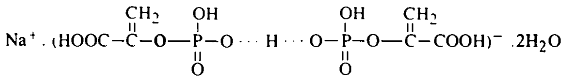
(*Received 12 April 1996; accepted 5 June 1996*)

Abstract

The crystal structures of two new salts of phosphoenolpyruvic acid (H_3PEP), sodium hydrogen bis[2-(phosphonooxy)propenoate, $Na^+.C_6H_9O_{12}P_2^-.2H_2O$, (I), and potassium hydrogen bis[2-(phosphonooxy)propenoate, $K^+.C_3H_4O_6P^-.C_3H_5O_6P$, (II), have been determined. In the crystal of (I), the phosphate groups of two PEP residues related by a center of symmetry are joined by a very short disordered hydrogen bond with an O···O distance of 2.456 (2) Å. As a result, the bis(phosphoenolpyruvate) monoanion can be distinguished. Crystals of (I) are almost isomorphous with crystals of zinc(II), manganese(II), magnesium and calcium bis(phosphoenolpyruvate) dihydrate and zinc(II) bis(phosphoglycolate) dihydrate. The crystal of (II) was found to be the 1:1 salt co-crystallized with the un-ionized molecular acid in the crystal chemical unit $K^+.H_2PEP^-.H_3PEP$. The P—O(ester) bond in the acid molecule [1.578 (2) Å] is shorter than in the monoanion [1.618 (2) Å]. In the sodium salt, this bond is 1.612 (2) Å. In both crystals, there are networks of strong hydrogen bonds.

Comment

This investigation was undertaken as part of a study of the structure of the phosphoenolpyruvate (PEP) moiety which may exist formally in four different forms, the tribasic acid, the monoanion, the dianion and the trianion. All of these forms have been characterized in the crystalline state (Weichsel & Lis, 1994; Souhassou, Schaber & Blessing, 1996). However, in the case of ammonium it is possible to obtain an acid salt, ammonium hydrogen bis(phosphoenolpyruvate) (Weichsel, Lis & Kuczek, 1991), and we report here the structures of two further salts of similar stoichiometry, $NaH_5(PEP)_2.2H_2O$, (I), and $KH_5(PEP)_2$, (II).



$$Na^+ . (HOOC-\overset{CH_2}{\overset{\|}{C}}-O-\overset{OH}{\overset{|}{\underset{\underset{O}{\|}}{P}}}-O\cdots H\cdots O-\overset{OH}{\overset{|}{\underset{\underset{O}{\|}}{P}}}-O-\overset{CH_2}{\overset{\|}{C}}-COOH)^- .2H_2O$$

(I)

$$K^+ \quad . \quad O=\overset{O^-}{\overset{|}{\underset{\underset{OH}{|}}{P}}}-O-\overset{CH_2}{\overset{\|}{C}}-COOH \quad . \quad O=\overset{OH}{\overset{|}{\underset{\underset{OH}{|}}{P}}}-O-\overset{CH_2}{\overset{\|}{C}}-COOH$$

(II)

In the crystal of (I), the phosphate groups of two PEP residues related by a center of symmetry are joined by a very short hydrogen bond with an O···O distance of 2.456 (2) Å. As a result, the bis(phosphoenolpyruvate) monoanion may be distinguished with a symmetric hydrogen bond of equivalent double minima. However, since the bridging H3 atom is disordered, it may be also concluded that the crystal is built up of disordered acid molecules and phosphoenolpyruvate monoanions bridged by short hydrogen bonds. In such a case, the bond lengths in the phosphate group (Table 2) would be averaged values for these two PEP species. The enolpyruvate system is not quite planar, the angle between the carboxyl plane (C1, O5 and O6) and that formed by atoms C2, C3 and O4 being 2.9 (3)°.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

The packing of the crystal is shown in Fig. 2. The Na^+ cations are located at the centers of distorted octahedra formed by two water and four phosphate O atoms. These octahedra are doubly connected in the [010] direction by phosphate O atoms, forming a linear polymer. The hydrogen-bond distances and angles are listed in Table 3; the O1—H1 hydroxyl group is involved (as donor) with a water molecule, and pairs of centrosymmetrically related carboxylic groups interact with each other in the usual way. Furthermore, the water H atom H72 forms a hydrogen bond with the phosphate atom O2 and the second water H atom (H71) is involved in a weak hydrogen bond. The unit-cell parameters and the atomic coordinates of most of the atoms show that the present crystal is almost isomorphous with M^{II} bis(phosphoenolpyruvate) dihydrate, where M^{II} = Ca, Mg, Zn or Mn (Lis, 1992) and with zinc(II) bis(phosphoglycolate) dihydrate (Lis, 1994).

The asymmetric unit of crystal (II) contains a phosphoenolpyruvic acid molecule (Fig. 3*a*), a phosphoenolpyruvate monoanion (Fig. 3*b*) and a K^+ cation, while that of ammonium bis(phosphoenolpyruvate) comprises two pairs of acid molecules and monoanions (Weichsel, Lis & Kuczek, 1991). The acid molecule and monoanion differ in the orientations of the

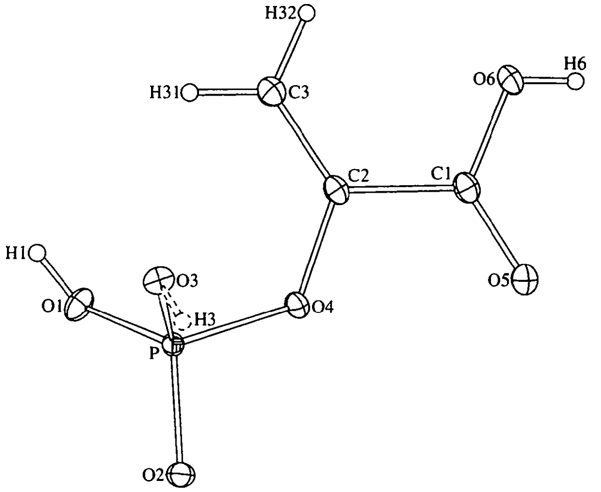


Fig. 1. The structure and numbering scheme of the phosphoenolpyruvate residue in the sodium salt, (I). The disordered H3 atom has occupancy factor 0.5. Displacement ellipsoids are shown at the 50% probability level.

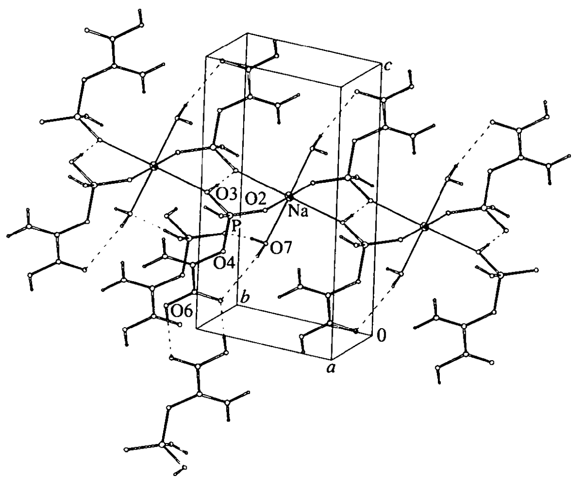
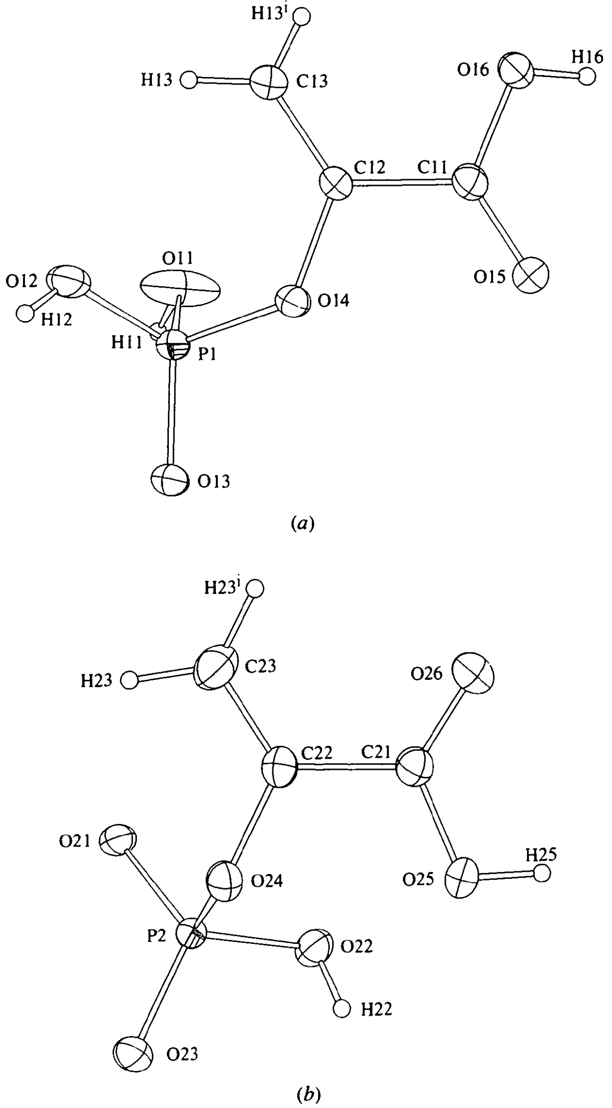


Fig. 2. The packing in (I); dashed lines denote hydrogen bonds. Only half of the disordered H3 atoms are shown.



(*a*)

(*b*)

Fig. 3. The molecular structure of the phosphoenolpyruvic acid molecule (*a*) and phosphoenolpyruvate monoanion (*b*) in the potassium salt (II). Only the major component of the disordered atom P2 is shown. Displacement ellipsoids are drawn at the 50% probability level.

phosphate group with respect to the pyruvate backbone (Fig. 3 and Table 5). The carboxylic hydroxyl is *syn* planar to the terminal $=CH_2$ group in the acid molecule, but is *trans* planar in the monoanion. The different positions of the hydroxyl O atoms in the carboxyl group were observed previously by us in other PEP moieties (Weichsel & Lis, 1994). The enolpyruvate system is not a rigid group; the angle between the carboxyl group and the plane through C12, C13 and O14 (C22, C23 and O24 for the monoanion) is 0.7 (3)° for the acid [10.1 (2)° for the monoanion]. The phosphate group in the acid molecule lies almost *trans* to the carboxylic group (Fig. 3*a*); the P1—O14—C12—C13 and P1—O14—C12—C11 torsion angles are 36.0 (4) and −143.2 (2)°, respectively. The P—O(ester) bond length of 1.578 (2) Å is similar to those found previously in crystals of phosphoenolpyruvic acid (Weichsel, Lis & Kuczek, 1989), and a little shorter than those found in the acid molecules of ammonium hydrogen bis-(phospenolpyruvate) (Weichsel, Lis & Kuczek, 1991). In the monoanion, the phosphate group is almost perpendicular to the enolpyruvate moiety as shown by the P2—O24—C22—C23 and P2—O24—C22—C21 torsion angles of 94.3 (3) and −89.9 (3)°, respectively. Both PEP species are interbridged by hydrogen bonds (Table 6), some of them relatively strong. The carboxylic O atom O16 forms (as donor) a hydrogen bond with the phosphate atom O21, while O22 and O25 form (as donors) hydrogen bonds with atoms O13 and O15, respectively, generated by the 2_1 screw axis. Two other hydrogen bonds (involving atoms related by the *n* glide plane) are formed between O11 (as donor) with O23 and O12 (as donor) with O21. The K^+ cation is octacoordinate, with K···O distances of 2.714 (2)–3.203 (2) Å to three carbonyl and five phosphate O atoms (Table 5). Each K^+ ion is coordinated to seven independent PEP moieties.

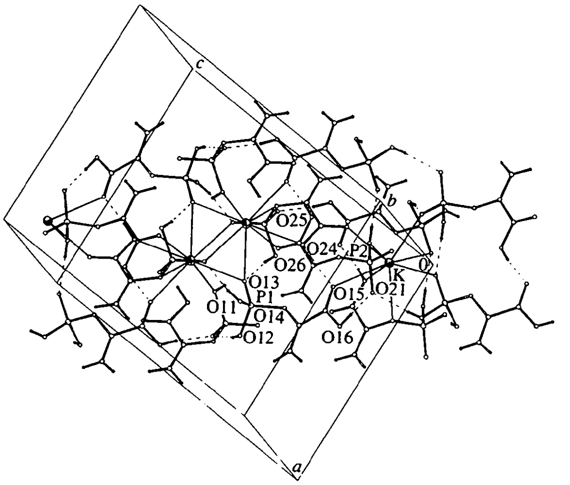


Fig. 4. The packing in (II). Only the major components of the disordered atoms K and P2 are shown.

Experimental

Colorless crystals of the title compounds (I) and (II) were obtained by slow concentration of aqueous solutions of phosphoenolpyruvic acid (Weichsel, Lis, & Kuczek, 1989) and $NaHCO_3$ or $KHCO_3$, respectively, in approximate stoichiometric ratios.

Compound (I)

Crystal data

$Na^+.C_6H_9O_{12}P_2^-.2H_2O$
$M_r = 394.09$
Triclinic
$P\overline{1}$
$a = 5.395\ (3)$ Å
$b = 5.742\ (2)$ Å
$c = 11.428\ (4)$ Å
$\alpha = 82.06\ (3)°$
$\beta = 87.64\ (4)°$
$\gamma = 83.32\ (4)°$
$V = 348.1\ (3)$ Å^3
$Z = 1$
$D_x = 1.880\ (2)$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 60 reflections
$\theta = 10–15°$
$\mu = 0.422$ mm^{-1}
$T = 85\ (2)$ K
Tablet
0.4 × 0.4 × 0.15 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3299 measured reflections
2024 independent reflections
1808 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0197$
$\theta_{\rm max} = 30°$
$h = -7 \rightarrow 3$
$k = -8 \rightarrow 8$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0265$
$wR(F^2) = 0.0741$
$S = 1.128$
2024 reflections
134 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 0.09P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.098$
$\Delta\rho_{\rm max} = 0.61$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (I)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Na	1/2	1/2	1/2	0.0113 (2)
P	0.23317 (4)	1.00821 (4)	0.35084 (2)	0.0068 (1)
O1	−0.01990 (14)	1.14547 (14)	0.31174 (7)	0.0115 (2)
O2	0.20588 (14)	0.75680 (13)	0.39516 (7)	0.0098 (2)
O3	0.36519 (14)	1.13955 (13)	0.43234 (7)	0.0098 (2)
O4	0.40166 (15)	0.99648 (13)	0.23155 (7)	0.0110 (2)
O5	0.79159 (15)	0.88861 (14)	0.09730 (8)	0.0142 (2)
O6	0.84149 (16)	1.27148 (15)	0.03996 (7)	0.0138 (2)

O7	0.80999 (15)	0.56746 (14)	0.34360 (7)	0.0113 (2)
C1	0.7282 (2)	1.1006 (2)	0.09885 (9)	0.0102 (2)
C2	0.5060 (2)	1.1855 (2)	0.16960 (9)	0.0094 (2)
C3	0.4259 (2)	1.4139 (2)	0.16831 (10)	0.0120 (2)

Table 2. *Selected geometric parameters (Å, °) for (I)*

P—O1	1.545 (2)	Na···O2	2.292 (2)
P—O2	1.484 (2)	Na···O7	2.420 (2)
P—O3	1.522 (2)	Na···O3^{i}	2.500 (2)
P—O4	1.612 (2)		
O1—P—O2	111.2 (1)	O3—P—O4	107.9 (1)
O1—P—O3	111.4 (1)	O2—Na—O7	91.2 (1)
O1—P—O4	105.7 (1)	O2—Na—O3^{i}	85.6 (1)
O2—P—O3	115.6 (1)	O7—Na—O3^{i}	84.3 (1)
O2—P—O4	104.1 (1)		
O1—P—O4—C2	72.9 (1)	P—O4—C2—C3	−25.1 (2)
O2—P—O4—C2	−169.8 (1)	P—O4—C2—C1	155.8 (1)
O3—P—O4—C2	−46.4 (1)		

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

Table 3. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O3^{i}	0.79 (4)	1.66 (4)	2.456 (2)	178 (5)
O6—H6···O5^{ii}	0.75 (3)	1.89 (3)	2.635 (2)	178 (3)
O1—H1···O7^{iii}	0.77 (3)	1.79 (3)	2.558 (2)	172 (3)
O7—H71···O5	0.80 (3)	2.41 (3)	3.143 (2)	153 (3)
O7—H72···O2^{iv}	0.84 (3)	1.79 (3)	2.629 (2)	172 (3)

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

Compound (II)

Crystal data

$K^+.C_3H_4O_6P^-.C_3H_5O_6P$
$M_r = 374.17$
Monoclinic
$P2_1/n$
$a = 11.927\ (7)$ Å
$b = 6.803\ (4)$ Å
$c = 17.215\ (11)$ Å
$\beta = 101.91\ (5)°$
$V = 1367\ (2)$ Å^3
$Z = 4$
$D_x = 1.818\ (3)$ Mg m^{-3}
$D_m = 1.77$ Mg m^{-3}
D_m measured by flotation in CCl_4/1,2-dibromoethane at room temperature
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 9–13°$
$\mu = 0.683$ mm^{-1}
$T = 150\ (2)$ K
Columnar
0.5 × 0.2 × 0.1 mm
Colorless

Data collection

Kuma KM-4 automatic diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3676 measured reflections
3543 independent reflections
2272 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0391$
$\theta_{\rm max} = 30°$
$h = -16 \rightarrow 1$
$k = 0 \rightarrow 9$
$l = -23 \rightarrow 24$
3 standard reflections monitored every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0361$
$wR(F^2) = 0.0954$
$S = 1.129$
3543 reflections
235 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.077$
$\Delta\rho_{\rm max} = 0.82$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.46$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
K†	0.11613 (4)	0.15807 (8)	0.08409 (3)	0.0180 (2)
K1‡	0.113 (2)	0.348 (4)	0.0846 (13)	0.021 (5)
P1	0.60334 (5)	0.30302 (10)	0.35052 (4)	0.0173 (2)
O11	0.6311 (3)	0.5164 (4)	0.33225 (15)	0.0415 (7)
O12	0.7149 (2)	0.1871 (5)	0.35865 (14)	0.0451 (8)
O13	0.5430 (2)	0.2784 (3)	0.41716 (10)	0.0200 (4)
O14	0.5213 (2)	0.2293 (3)	0.27199 (10)	0.0215 (4)
O15	0.3392 (2)	0.2994 (3)	0.15866 (11)	0.0221 (4)
O16	0.4450 (2)	0.3240 (3)	0.06620 (11)	0.0228 (4)
C11	0.4317 (2)	0.2959 (4)	0.13893 (14)	0.0174 (5)
C12	0.5408 (2)	0.2581 (4)	0.19644 (14)	0.0175 (5)
C13	0.6422 (3)	0.2555 (6)	0.1768 (2)	0.0303 (7)
P2†	0.19262 (5)	0.66109 (10)	0.00837 (4)	0.0143 (2)
P21‡	0.194 (2)	0.846 (4)	0.0087 (13)	0.011 (5)
O21	0.2731 (2)	0.5137 (3)	−0.01501 (10)	0.0185 (4)
O22	0.1287 (2)	0.5589 (3)	0.06778 (11)	0.0190 (4)
O23	0.1114 (2)	0.7604 (3)	−0.05668 (11)	0.0226 (4)
O24	0.2667 (2)	0.8380 (3)	0.05666 (11)	0.0188 (4)
O25	0.2121 (2)	0.8508 (3)	0.19680 (11)	0.0228 (4)
O26	0.3848 (2)	0.7465 (4)	0.26122 (12)	0.0282 (5)
C21	0.3198 (3)	0.7946 (4)	0.20090 (15)	0.0189 (5)
C22	0.3542 (2)	0.7996 (4)	0.12243 (15)	0.0188 (5)
C23	0.4618 (3)	0.7818 (5)	0.1156 (2)	0.0269 (6)

† Site occupancy = 0.973(2). ‡ Site occupancy = 0.027(2).

Table 5. *Selected geometric parameters (Å, °) for (II)*

P1—O11	1.536 (3)	K···O13^{i}	3.203 (2)
P1—O12	1.528 (3)	K···O13^{ii}	2.859 (2)
P1—O13	1.484 (2)	K···O15	2.871 (3)
P1—O14	1.578 (2)	K···O22	2.749 (3)
P2—O21	1.500 (2)	K···O23^{iii}	2.714 (2)
P2—O22	1.559 (2)	K···O24^{iv}	2.922 (2)
P2—O23	1.484 (2)	K···O25^{iv}	2.920 (2)
P2—O24	1.618 (2)	K···O26^{i}	2.732 (2)
O11—P1—O12	106.6 (2)	O21—P2—O22	107.7 (2)
O11—P1—O13	115.1 (2)	O21—P2—O23	117.2 (2)
O11—P1—O14	104.3 (2)	O21—P2—O24	108.9 (2)
O12—P1—O13	115.0 (2)	O22—P2—O23	111.5 (2)
O12—P1—O14	106.8 (2)	O22—P2—O24	106.5 (2)
O13—P1—O14	108.2 (2)	O23—P2—O24	104.6 (2)
O11—P1—O14—C12	46.3 (3)	O21—P2—O24—C22	−53.2 (2)
O12—P1—O14—C12	−66.3 (3)	O22—P2—O24—C22	62.7 (2)
O13—P1—O14—C12	169.3 (2)	O23—P2—O24—C22	−179.1 (2)
P1—O14—C12—C13	36.0 (4)	P2—O24—C22—C23	94.3 (3)
P1—O14—C12—C11	−143.2 (2)	P2—O24—C22—C21	−89.9 (3)

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

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O22—H22···O13^{v}	0.80 (5)	1.80 (5)	2.590 (3)	171 (5)
O25—H25···O15^{v}	0.91 (4)	1.81 (4)	2.705 (3)	169 (4)
O11—H11···O23^{vi}	0.75 (4)	1.74 (4)	2.491 (3)	171 (4)
O12—H12···O21^{vii}	0.67 (5)	1.87 (5)	2.541 (3)	171 (6)
O16—H16···O21	0.83 (5)	1.74 (5)	2.576 (3)	173 (5)

Symmetry codes: (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

The Na crystals were unstable in air and therefore the X-ray data collection was performed at 85 K. [The crystal data for (I) at 294 (2) K are: a = 5.415 (2), b = 5.782 (2), c = 11.634 (4) Å, α = 82.22 (3), β = 87.24 (3), γ = 83.08 (3)°, V = 358.1 (3) Å^3, D_x = 1.827 (2) Mg m^{-3}.] The phosphate O3 atoms related by the center of symmetry were separated by rather the short distance of about 2.45 Å. The H-atom electron density associated with the center of symmetry showed two maxima in the difference map. During the refinement, a disordered model of the O—(H···H)—O bridge was attempted with an occupancy factor of 0.5 for H3.

The crystal data for the K$^+$ salt were initially measured at room temperature. [The crystal data for (II) at 296 (1) K are: a = 11.927 (9), b = 6.866 (6), c = 17.215 (12) Å, β = 102.19 (6)°, V = 1378 (2) Å^3, D_x = 1.803 (3) Mg m^{-3}.] On the final difference Fourier map, two relatively high peaks of 1.56 and 1.38 e Å^{-3} were observed near atoms K and P2, suggesting disorder which could not be resolved. Therefore, a second data set was collected at 150 K using another crystal. The starting refinement was with the room-temperature parameters, and the two relatively high peaks present in the difference map remained. They were interpreted as cooperative partial disorder of the K atom and the P2 phosphate group. The detailed nature of this phosphate-group disorder was not resolved and in the final refinement, the disorder was modeled only for K and P2 although the displacement parameters of O11 suggest that disorder may be present in the phosphate group centered on P1.

For both compounds, data collection: *Kuma KM-4 Software* (Kuma Diffraction, 1989); cell refinement: *Kuma KM-4 Software*; data reduction: *Kuma KM-4 Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

Financial support was received from KBN grant No. 2 P303 078 07.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kuma Diffraction (1989). *Kuma KM-4 User's Guide*. Version 3.1. Kuma Diffraction, Wrocław, Poland.
Lis, T. (1992). *Acta Cryst.* **C48**, 424–427.
Lis, T. (1994). *Acta Cryst.* **C50**, 181–185.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Souhassou, M., Schaber, P. M. & Blessing, R. H. (1996). *Acta Cryst.* **B51**, 865–875.
Weichsel, A. & Lis, T. (1994). *Pol. J. Chem.* **68**, 2079–2096.
Weichsel, A., Lis, T. & Kuczek, M. (1989). *Carbohydr. Res.* **194**, 63–70.
Weichsel, A., Lis, T. & Kuczek, M. (1991). *Acta Cryst.* **C47**, 2164–2167.

Acta Cryst. (1996). **C52**, 2724-2726

(Dimercaptomethylenepropanedinitrilato-*S*,*S'*)(pyridine)(triphenylphosphine)palladium(II)–Acetonitrile (1/1)

D.-L. LONG,[a] X.-Q. XIN[a] AND X.-Y. HUANG[b]

[a]*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China, and* [b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian 350002, People's Republic of China. E-mail: postchel@netra.nju.edu.cn*

(*Received 29 January 1996; accepted 21 March 1996*)

Abstract

In the structure of the title compound, [2,2-dimercapto-1,1-ethylenedicarbonitrilato(2−)-*S*,*S'*](pyridine-*N*)(triphenylphosphine-*P*)palladium(II)–acetonitrile (1/1), $[Pd(C_4N_2S_2)(C_5H_5N)(C_{18}H_{15}P)].CH_3CN$, the Pd atom is coordinated by the two S atoms of the dimercaptoethylenedicarbonitrilate ligand acting as a bidentate ligand, the P atom from triphenylphosphine and the N atom from pyridine, with Pd—S distances of 2.288 (2) and 2.340 (1) Å, a Pd—P distance of 2.300 (1) Å and a Pd—N distance of 2.082 (3) Å. The S—Pd—S angle is 75.35 (4)°.

Comment

Interest in palladium complexes is usually related to catalytic processes and their chemistry has been studied extensively. In a previous paper, we demonstrated the crystal and molecular structure of $[Pd(i\text{-mnt})_2]^{2-}$ (where i-mnt is dimercaptoethylenedicarbonitrilate or isomalononitriledithiolate) and its cluster-forming reaction with tetrathiotungstate (Long, Hou, Xin, Yu, Luo & Chen, 1996). In an effort to extend this field, we prepared $[(Ph_3P)_2Pd(i\text{-mnt})]$. When this compound