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, $\alpha = 82.22\,(3)$, $\beta = 87.24\,(3)$, $\gamma = 83.08\,(3)°$, $V = 358.1\,(3)$ 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, $\beta = 102.19\,(6)°$, $V = 1378\,(2)$ 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: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

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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.

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

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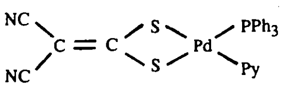
Abstract

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 was dissolved in acetonitrile to which a small amount of pyridine had been added, a substitution product, $[Pd(C_4N_2S_2)(C_{18}H_{15}P)(C_5H_5N)]$, (I), was obtained. This compound crystallizes with one acetonitrile solvent molecule per asymmetric unit.



(I)

The title complex is four-coordinate, with no close intermolecular contacts. The geometry about the Pd atom is distorted square planar. The largest deviation from the plane composed of Pd and its four donor atoms is 0.1293 (10) Å for S2. The S1—Pd—S2 bond angle [75.35 (4)°] is restricted by the bite angle of the chelating ligand. The remaining angles in the square plane are correspondingly greater than 90°.

The geometry of the isomalononitriledithiolato ligand (i-mnt) is almost the same as that found in $[Pd(i\text{-}mnt)_2]^{2-}$ (Long *et al.*, 1996), where the ligand atoms are approximately planar except for the two S atoms, which deviate from the coordination plane by *ca* 0.1 Å; the dihedral angle between this plane and the PdS_2NP plane is *ca* 11°. It is possible for $d\pi(Pd)$–π^*(i-mnt) (metal-to-ligand change transfer) to take place. The S1—C6—S2 bond angle of 110.6 (2)° is equal to that found in $[Pd(i\text{-}mnt)_2]^{2-}$ and smaller than the value of 122.8 (3)° found in the sodium salt of i-mnt (Hummel, 1987). The C6—S1 and C6—S2 bond distances of 1.724 (4) and 1.716 (4) Å, respectively, are close to the values of 1.723 (3) and 1.725 (3) Å found in $[Pd(i\text{-}mnt)_2]^{2-}$. The difference between these two bond distances is attributed to the different coordination character of related Pd—S bonds.

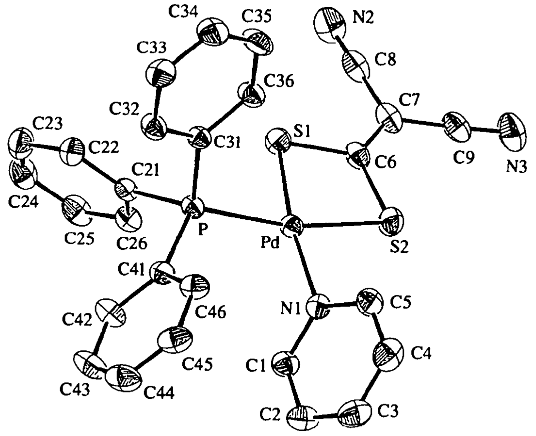


Fig. 1. View of the title compound with displacement ellipsoids shown at the 30% probability level and H atoms omitted for clarity.

The Pd—N bond distance of 2.082 (3) Å is typical for a Pd—N(sp^2) σ bond. The dihedral angle between the pyridine and PdS_2NP planes is 65.8 (3)°, indicating the absence of $d\pi(Pd)$–π^*(py) donation. The Pd—S2 bond is longer [2.340 (1) Å] than the Pd—S1 bond distance [2.288 (2) Å], indicating the greater *trans* influence of phosphorus compared with nitrogen donors. In the case of $[Pd(i\text{-}mnt)_2]^{2-}$, the two Pd—S distances are identical at 2.323 (1) Å.

Experimental

The title compound was obtained by the substitution reaction of $[Pd(PPh_3)_2(C_4N_2S_2)]$ with pyridine in acetonitrile. Single crystals were produced by slow evaporation of the solvent.

Crystal data

$[Pd(C_4N_2S_2)(C_5H_5N)$-
$(C_{18}H_{15}P)].C_2H_3N$
$M_r = 629.02$
Triclinic
$P\overline{1}$
$a = 9.733\ (1)$ Å
$b = 10.601\ (6)$ Å
$c = 13.835\ (4)$ Å
$\alpha = 93.56\ (2)°$
$\beta = 94.94\ (2)°$
$\gamma = 94.31\ (3)°$
$V = 1415\ (2)$ Å^3
$Z = 2$
$D_x = 1.48$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.06$–$14.93°$
$\mu = 0.868$ mm^{-1}
$T = 296$ K
Needle
0.90 × 0.25 × 0.15 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scans (*TEXSAN*; Molecular Structure Corporation, 1987)
$T_{min} = 0.73$, $T_{max} = 0.88$
4979 measured reflections
4979 independent reflections

4417 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 300 reflections
intensity decay: 1.1%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.048$
$S = 1.35$
4417 reflections
334 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = 0.05$

$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -1.12$ e Å^{-3} (near Pd)
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Pd	0.22769 (3)	0.03259 (2)	0.07635 (2)	2.96 (1)
S1	0.2691 (1)	0.23810 (9)	0.03820 (6)	3.92 (4)
S2	0.2819 (1)	0.0172 (1)	−0.08529 (7)	4.34 (4)
P	0.20458 (9)	0.08660 (8)	0.23738 (6)	2.87 (3)
N1	0.1921 (3)	−0.1621 (3)	0.0864 (2)	3.3 (1)
N2	0.3654 (4)	0.4975 (4)	−0.1228 (3)	6.2 (2)
N3	0.4318 (5)	0.1614 (4)	−0.3049 (3)	6.6 (2)
C1	0.0679 (4)	−0.2152 (3)	0.1034 (3)	3.8 (1)
C2	0.0423 (4)	−0.3439 (4)	0.1094 (3)	4.7 (2)
C3	0.1472 (5)	−0.4206 (4)	0.0990 (3)	5.3 (2)
C4	0.2746 (5)	−0.3668 (4)	0.0813 (3)	5.3 (2)
C5	0.2951 (4)	−0.2381 (4)	0.0756 (3)	4.2 (2)
C6	0.3062 (3)	0.1797 (4)	−0.0749 (3)	3.6 (1)
C7	0.3488 (4)	0.2552 (4)	−0.1466 (3)	4.1 (2)
C8	0.3578 (4)	0.3889 (4)	−0.1329 (3)	4.6 (2)
C9	0.3929 (4)	0.2012 (4)	−0.2336 (3)	4.5 (2)
C21	0.1018 (3)	0.2225 (3)	0.2533 (2)	3.2 (1)
C22	0.1193 (4)	0.3032 (4)	0.3367 (3)	4.1 (2)
C23	0.0325 (5)	0.4000 (4)	0.3478 (3)	5.0 (2)
C24	−0.0705 (5)	0.4159 (4)	0.2765 (3)	5.0 (2)
C25	−0.0881 (4)	0.3361 (4)	0.1933 (3)	4.7 (2)
C26	−0.0018 (4)	0.2392 (3)	0.1814 (3)	3.8 (1)
C31	0.3727 (3)	0.1258 (3)	0.3043 (2)	3.0 (1)
C32	0.3914 (4)	0.1282 (4)	0.4053 (2)	3.8 (1)
C33	0.5215 (4)	0.1573 (4)	0.4532 (3)	4.6 (2)
C34	0.6330 (4)	0.1833 (5)	0.4019 (3)	5.2 (2)
C35	0.6158 (4)	0.1815 (5)	0.3028 (3)	5.5 (2)
C36	0.4863 (4)	0.1523 (4)	0.2536 (3)	4.2 (2)
C41	0.1235 (3)	−0.0355 (3)	0.3051 (2)	3.3 (1)
C42	−0.0114 (4)	−0.0319 (4)	0.3297 (3)	4.7 (2)
C43	−0.0706 (5)	−0.1316 (5)	0.3777 (4)	5.9 (2)
C44	0.0021 (5)	−0.2334 (5)	0.3981 (3)	5.7 (2)
C45	0.1341 (5)	−0.2383 (4)	0.3728 (3)	5.0 (2)
C46	0.1963 (4)	−0.1398 (4)	0.3269 (3)	4.0 (1)
N4	0.2955 (7)	0.4466 (6)	0.5565 (5)	10.1 (3)
C10	0.5278 (7)	0.5003 (6)	0.6547 (5)	8.6 (3)
C11	0.3964 (7)	0.4700 (6)	0.5997 (4)	7.2 (3)

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

Pd—N1	2.082 (3)	P—C21	1.828 (3)
Pd—S1	2.288 (2)	N1—C1	1.341 (5)
Pd—S2	2.340 (1)	N1—C5	1.344 (5)
Pd—P	2.300 (1)	N2—C8	1.146 (6)
S1—C6	1.724 (4)	N3—C9	1.154 (5)
S2—C6	1.716 (4)	C6—C7	1.385 (5)
P—C31	1.816 (3)	C7—C8	1.414 (6)
P—C41	1.817 (3)	C7—C9	1.414 (6)
N1—Pd—S1	170.38 (8)	C6—S2—Pd	86.2 (1)
N1—Pd—S2	95.13 (8)	S2—C6—S1	110.6 (2)
N1—Pd—P	95.57 (8)	C6—C7—C8	121.2 (4)
S1—Pd—P	94.04 (4)	C6—C7—C9	121.0 (4)
S1—Pd—S2	75.35 (4)	C8—C7—C9	117.7 (3)
S2—Pd—P	167.89 (3)	N2—C8—C7	179.2 (5)
C6—S1—Pd	87.7 (1)	N3—C9—C7	177.4 (5)

Data were collected with a scan speed of $< 5.49°\ \mathrm{min}^{-1}$ and an ω-scan width of $(0.45 + 0.35\tan\theta)°$. The structure was solved by direct methods, the Pd atom being located in the E map and the remaining non-H atoms being deduced from successive difference Fourier syntheses. The structure was refined by full-matrix least-squares techniques. H atoms were positioned geometrically and not refined. All calculations were performed on a MicroVAX 3100 computer using the *TEXSAN* (Molecular Structure Corporation, 1987) program package.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Hydroxy-2,1λ⁵-benzoxarsol-3-one Monohydrate

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Abstract

The stereochemistry around arsenic in the title compound, 1-hydroxybenz[*c*][1,2]oxarsol-3-one monohydrate, $C_7H_5AsO_3.H_2O$, is distorted trigonal bipyramidal, with the carboxylate O atom and the water molecule occupying apical positions, and the phenyl C atom, the hydroxyl group and the lone pair occupying equatorial positions. The formation of a bond between the As and