(Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1387). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[1,3-Bis(diphenylphosphino)propane-*P*,*P*′](1,3-propanedithiolato-*S*,*S*′)palladium(II) Acetonitrile Solvate, [Pd{$Ph_2P(CH_2)_3PPh_2$}(SC_3H_6S)].CH_3CN

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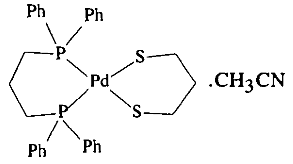
Abstract

The structure of the title compound, [Pd($C_3H_6S_2$)($C_{27}H_{26}P_2$)].CH_3CN, consists of discrete mononuclear palladium(II) complex and acetonitrile molecules. The Pd atom is fourfold coordinated by two P atoms from the phosphine ligand and two S atoms from the $C_3H_6S_2^{2-}$ ligand in a distorted square-planar geometry. The average Pd—S and Pd—P distances are 2.326 (8) and 2.299 (7) Å, respectively.

Comment

Transition metal compounds with mixed sulfur and phosphine ligands have attracted much attention due to their importance in a wide range of chemical and industrial systems. In the nickel-group metals, many nickel compounds with such mixed ligands have been reported. Surprisingly few palladium compounds, such as [$Pd_2(SC_6F_5)_2(PPh_3)_2$] (Fenn & Segrott, 1972), have been structurally characterized. We reported recently the palladium compounds [Pd($SCH_2CH_2SCH_2CH_2S$)(PPh_3)$_2$] and [$Pd_2(PPh_3)_2(HOC_6H_4S)_2Cl_2$] (Cao, Hong, Jiang, Xie & Liu, 1996), and [$Pd_2(PPh_3)_2(SC_2H_4S)_2$] (Cao, Hong, Jiang & Liu, 1995). We report here the crystal structure of a mononuclear palladium complex, namely, [Pd{$Ph_2P(CH_2)_3PPh_2$}(SC_3H_6S)].CH_3CN, (I).



(I)

The title compound, (I), consists of a discrete mononuclear palladium(II) complex and an acetonitrile molecule (Fig. 1). The Pd atom is fourfold coordinated by two P atoms from the phosphine ligand and two S atoms from the $C_3H_6S_2^{2-}$ ligand in a distorted square-planar geometry. The displacements from the least-squares plane formed by the atoms Pd(1), P(1), P(2), S(1) and S(2) are 0.007, −0.067, 0.064, −0.65 and

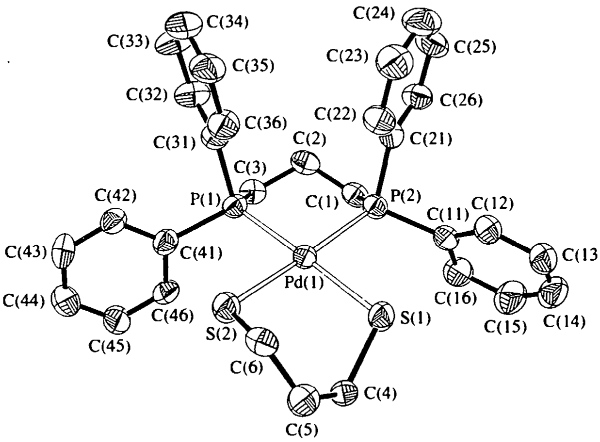


Fig. 1. The crystal structure of the title complex with ellipsoids drawn at the 30% probability level.

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0.062 Å, respectively. The Pd(1)—P(1)—C(3)—C(2)—C(1)—P(2) ring is in a chair form, whereas the Pd(1)—S(1)—C(4)—C(5)—C(6)—S(2) ring has a twisted boat conformation. The average Pd—S and Pd—P distances are 2.326 (8) and 2.299 (7) Å, respectively.

Experimental

The title compound was obtained from the reaction of $\mathrm{PdCl_2}$, $\mathrm{Ph_2P(CH_2)_3PPh_2}$ and $\mathrm{Na_2SC_3H_6S}$ (molar ratio 1:1:1) in MeOH, and recrystallized from $\mathrm{CH_3CN}$ solution.

Crystal data

$[\mathrm{Pd}(\mathrm{C_3H_6S_2})(\mathrm{C_{27}H_{26}P_2})].\mathrm{CH_3CN}$
$M_r = 666.1$
Monoclinic
$P2_1/c$
$a = 10.113\ (2)$ Å
$b = 16.951\ (3)$ Å
$c = 18.015\ (4)$ Å
$\beta = 98.49\ (3)^\circ$
$V = 3054.6$ Å^3
$Z = 4$
$D_x = 1.450$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 58 reflections
$\theta = 9$–14°
$\mu = 0.871$ mm^{-1}
$T = 294$ K
Prism
0.40 × 0.20 × 0.20 mm
Yellow

Data collection

Rigaku R-axis II diffractometer
ω scans
Absorption correction: none
5686 measured reflections
5361 independent reflections

3863 observed reflections [$F > 4\sigma(F)$]
$R_{\mathrm{int}} = 0.0224$
$\theta_{\mathrm{max}} = 22.5^\circ$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 20$
$l = -21 \rightarrow 21$
No standard reflections

Refinement

Refinement on F
$R = 0.035$
$wR = 0.048$
$S = 1.12$
3863 reflections
343 parameters
$w = 1/[\sigma^2(F) + 0.00484F^2]$
$(\Delta/\sigma)_{\mathrm{max}} = 0.18$

$\Delta\rho_{\mathrm{max}} = 0.98$ e Å^{-3}
$\Delta\rho_{\mathrm{min}} = -0.73$ e Å^{-3}
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 (Å^2)*

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

	x	y	z	U_{eq}
Pd(1)	0.1350 (1)	0.0129 (1)	0.2127 (1)	0.044 (1)
P(1)	0.0539 (1)	0.0077 (1)	0.3249 (1)	0.050 (1)
P(2)	0.0401 (1)	−0.1071 (1)	0.1757 (1)	0.050 (1)
S(1)	0.2282 (2)	0.0132 (1)	0.1028 (1)	0.065 (1)
S(2)	0.2192 (1)	0.1372 (1)	0.2503 (1)	0.067 (1)
C(1)	0.0523 (5)	−0.1791 (3)	0.2516 (2)	0.057 (2)
C(2)	−0.0154 (5)	−0.1549 (3)	0.3178 (3)	0.062 (2)
C(3)	0.0580 (5)	−0.0907 (3)	0.3672 (2)	0.058 (2)
C(4)	0.3794 (7)	0.0741 (4)	0.1249 (4)	0.045 (2)
C(5)	0.3598 (6)	0.1587 (3)	0.1277 (3)	0.089 (3)
C(6)	0.2380 (8)	0.1859 (5)	0.1593 (4)	0.055 (2)
C(11)	0.1054 (5)	−0.1572 (3)	0.0991 (3)	0.055 (2)
C(12)	0.0556 (5)	−0.1363 (3)	0.0255 (3)	0.068 (2)
C(13)	0.1124 (6)	−0.1702 (4)	−0.0333 (3)	0.082 (2)
C(14)	0.2145 (7)	−0.2227 (4)	−0.0202 (4)	0.096 (3)
C(15)	0.2631 (7)	−0.2433 (4)	0.0525 (4)	0.095 (3)
C(16)	0.2098 (5)	−0.2103 (3)	0.1127 (3)	0.078 (2)
C(21)	−0.1383 (4)	−0.1024 (3)	0.1408 (3)	0.054 (2)
C(22)	−0.1925 (5)	−0.0315 (3)	0.1140 (3)	0.068 (2)
C(23)	−0.3265 (6)	−0.0267 (4)	0.0840 (3)	0.089 (3)
C(24)	−0.4064 (6)	−0.0931 (4)	0.0806 (3)	0.093 (3)
C(25)	−0.3511 (6)	−0.1630 (4)	0.1067 (3)	0.089 (3)
C(26)	−0.2179 (5)	−0.1686 (3)	0.1365 (3)	0.070 (2)
C(31)	−0.1178 (5)	0.0417 (3)	0.3205 (3)	0.059 (2)
C(32)	−0.1999 (5)	0.0194 (4)	0.3719 (3)	0.079 (2)
C(33)	−0.3274 (6)	0.0488 (4)	0.3674 (4)	0.098 (3)
C(34)	−0.3759 (6)	0.1004 (4)	0.3101 (4)	0.095 (3)
C(35)	−0.2958 (5)	0.1243 (4)	0.2598 (3)	0.080 (2)
C(36)	−0.1670 (5)	0.0946 (3)	0.2648 (3)	0.068 (2)
C(41)	0.1478 (4)	0.0654 (3)	0.4009 (2)	0.054 (2)
C(42)	0.0908 (5)	0.1282 (3)	0.4347 (2)	0.058 (2)
C(43)	0.1671 (6)	0.1714 (3)	0.4899 (3)	0.069 (2)
C(44)	0.2981 (6)	0.1530 (3)	0.5124 (3)	0.075 (2)
C(45)	0.3554 (5)	0.0922 (3)	0.4792 (3)	0.076 (2)
C(46)	0.2810 (5)	0.0476 (3)	0.4234 (3)	0.066 (2)
N(1)	0.3955 (6)	0.8426 (5)	0.3594 (4)	0.127 (3)
C(7)	0.4370 (6)	0.8663 (4)	0.3112 (4)	0.085 (3)
C(8)	0.4889 (9)	0.8975 (6)	0.2484 (4)	0.145 (4)

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

Pd(1)—P(1)	2.292 (1)	P(2)—C(11)	1.825 (5)
Pd(1)—P(2)	2.305 (1)	P(2)—C(21)	1.823 (5)
Pd(1)—S(1)	2.316 (2)	S(1)—C(4)	1.839 (7)
Pd(1)—S(2)	2.335 (1)	S(2)—C(6)	1.870 (8)
P(1)—C(3)	1.831 (5)	C(1)—C(2)	1.516 (7)
P(1)—C(31)	1.821 (5)	C(2)—C(3)	1.527 (6)
P(1)—C(41)	1.831 (4)	C(4)—C(5)	1.450 (9)
P(2)—C(1)	1.824 (5)		
P(1)—Pd(1)—P(2)	91.9 (1)	Pd(1)—P(2)—C(11)	116.6 (2)
P(1)—Pd(1)—S(1)	176.3 (1)	C(1)—P(2)—C(11)	105.2 (2)
P(2)—Pd(1)—S(1)	87.6 (1)	Pd(1)—P(2)—C(21)	114.2 (2)
P(1)—Pd(1)—S(2)	86.7 (1)	C(1)—P(2)—C(21)	104.0 (2)
P(2)—Pd(1)—S(2)	176.8 (1)	C(11)—P(2)—C(21)	102.1 (2)
S(1)—Pd(1)—S(2)	94.0 (1)	Pd(1)—S(1)—C(4)	104.2 (2)
Pd(1)—P(1)—C(3)	114.4 (2)	Pd(1)—S(2)—C(6)	102.9 (2)
Pd(1)—P(1)—C(31)	114.4 (2)	P(2)—C(1)—C(2)	114.9 (3)
C(3)—P(1)—C(31)	105.7 (2)	C(1)—C(2)—C(3)	114.4 (4)
Pd(1)—P(1)—C(41)	115.2 (2)	P(1)—C(3)—C(2)	115.3 (3)
C(3)—P(1)—C(41)	101.4 (2)	S(1)—C(4)—C(5)	116.7 (5)
C(31)—P(1)—C(41)	104.4 (2)	C(4)—C(5)—C(6)	116.1 (6)
Pd(1)—P(2)—C(1)	113.2 (1)	S(2)—C(6)—C(5)	113.0 (5)

Determination of the cell constants and data collection were carried out at room temperature on a Rigaku R-axis II Image-Plate diffractometer (Sato, Yamamoto, Imada, Katsube, Tanaka & Higashi, 1992) by taking oscillation photographs (total oscillation range 0–180°; 20 frames; oscillation angle 9° per frame; exposure time 10 min per frame). The structure was solved by Patterson methods. All non-H atoms were refined by full-matrix least-squares methods with anisotropic displacement parameters. H atoms were located at ideal positions and not refined. The H atoms of $\mathrm{CH_3CN}$ were not located. All calculations were performed on a 486 PC computer with the *SHELXTL-Plus* (Sheldrick, 1987) program package.

Data collection: Rigaku R-axis II software (Sato *et al.*, 1992). Cell refinement: Rigaku R-axis II software. Data reduction: Rigaku R-axis II software. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *LSFM* in *SHELXTL-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexaaquacobalt(II) Bis[(2-Hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetato)cobalt(III)]

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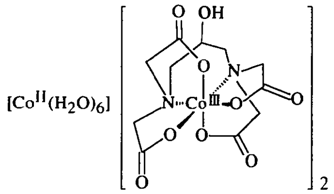
Abstract

The structure of the title complex, $[Co(H_2O)_6][Co(C_{11}H_{14}N_2O_9)]_2$, is comprised of discrete $[Co(hpdta)]^-$ anions (H_4hpdta is 2-hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid) and $[Co(H_2O)_6]^{2+}$ cations in a 2:1 molar ratio. The trivalent Co atom in the anion is coordinated by the hexadentate hpdta chelate ligand, with two amino-N atoms [Co—N 1.948 (3) Å] and four O atoms of the four monodentate carboxylato groups [Co—O 1.869 (2)–1.914 (2) Å] in a distorted octahedral arrangement, whereas the divalent Co atom in the cation is coordinated in an octahedral manner by six aqua ligands [Co—O 2.078 (2)–2.124 (2) Å]. The crystal structure is stabilized by extensive hydrogen bonding. Each aqua ligand forms two donor hydrogen bonds with the carboxyl O atoms from adjacent anions and the hydroxyl group forms a hydrogen bond with an adjacent carboxyl O atom.

Comment

2-Hydroxy-1,3-propanediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (H_4hpdta) is a structural analogue of the widely used chelate ligand ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid. Hence, it is somewhat surprising that metal complexes of H_4hpdta have received little attention. Only a few metal complexes of hpdta have been structurally characterized, including two cobalt(III) complexes (Kalina, Pavelčik & Majer, 1978; Sato & Yano, 1989) and one palladium(II) complex (Song, Zhang, Li, Jin & Jin, 1992). In this paper, we report the preparation and structure of a mixed-valent cobalt complex of hpdta, namely $[Co(H_2O)_6][Co(hpdta)]_2$, (I). The complex was obtained from a mixture of $Co(NO_3)_2$ and H_4hpdta in a weakly acidic aqueous solution.



(I)

The crystal structure of the mixed-valent complex comprises discrete $[Co(H_2O)_6]^{2+}$ cations and $[Co(hpdta)]^-$ anions in a 1:2 molar ratio. The Co^{III} atom in the anion is coordinated by a hexadentate hpdta chelate ligand, being surrounded by two N atoms [Co—N 1.948 (3) Å] and four O atoms from the four monodentate carboxylato groups [Co—O 1.869 (2)–1.914 (2) Å] in a distorted octahedral arrangement, with the most distorted bond angle being N1—Co1—N2 at 97.7 (1)° (Fig. 1). The bond lengths and angles of this anion are strikingly similar to those of the cobalt(III) complexes of hpdta reported previously (Kalina, Pavelčik & Majer, 1978; Sato & Yano, 1989). It is noteworthy that the Co1—O8 [1.869 (2) Å] and Co1—O4 [1.894 (2) Å] bonds are significantly shorter than the Co1—O2 [1.904 (2) Å] and Co1—O6 [1.914 (2) Å] bonds, which are *trans* with respect to the Co—N bonds, demonstrating clearly that nitrogen has a much greater *trans* effect than oxygen. In the $[Co(H_2O)_6]^{2+}$ cation, the Co^{II} atom is located at an inversion centre and is surrounded by six centrosymmetrically related aqua ligands [Co—O 2.078 (2)–2.124 (2) Å] in a slightly distorted octahedral