

The Crystal Structure of Dibromobis(diphenylphosphinoacetic acid)palladium(II)

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(Received 25 April 1978; accepted 11 October 1978)

Abstract

$C_{28}H_{26}Br_2O_4P_2Pd$, $PdBr_2(C_{14}H_{13}O_2P)_2$ is monoclinic, space group $P2_1/c$, with $a = 9.506$ (4), $b = 14.44$ (1), $c = 12.50$ (1) Å, $\beta = 120.98$ (5)°, $Z = 2$. The structure was refined to $R = 0.053$ for 1723 counter reflections [$I > 1.96\sigma(I)$]. The Pd atom is surrounded by two P [Pd–P 2.322 (2)] and two Br atoms [Pd–Br 2.447 (1) Å] in a *trans*-square-planar arrangement. In the axial positions of the distorted octahedron, carbonyl O atoms are located at a non-bonding distance of 3.171 (6) Å. The chains of molecules are connected by means of twofold hydrogen bonding between carboxyl groups [O–H...O 2.710 (7) Å].

Introduction

The title compound was studied as part of an investigation of transition-metal complexes of phosphinoacetic acid ligands. Depending on the metal ion and experimental conditions (pH, solvent), three bonding modes of the ligands were indicated by indirect methods: (a) through P alone, (b) through O alone, (c) chelating through O and P.

Experimental

The sample was prepared by reaction of Na_2PdBr_4 with diphenylphosphinoacetic acid in acetic acid solution (Růžičková & Podlahová, 1978). The cell dimensions were determined by the least-squares method from 15 reflections measured on an automatic Syntex $P2_1$ diffractometer (Cu $K\alpha$ radiation, graphite monochromator). Intensities were collected from a $0.10 \times 0.12 \times 0.15$ mm crystal for θ between 0 and 57.5°. $D_m = 1.703$ Mg m⁻³ was determined pycnometrically in water; $D_x = 1.704$ Mg m⁻³. The space group $P2_1/c$ was assumed from systematic absences: $h0l$, l odd; $0k0$, k odd. Only Lorentz–polarization corrections were applied ($\mu = 10.09$ mm⁻¹).

Structure determination

The positions of the Pd and Br atoms were obtained from a Patterson synthesis. The remaining non-H atoms were located by a Fourier synthesis and refined by the least-squares method to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.108$ with isotropic temperature factors. In further cycles the anisotropic temperature factors were refined to $R = 0.066$. The refinement was continued until the changes in the parameters were ≤ 0.3 of their e.s.d.'s. The positions of all H atoms were obtained from a difference synthesis. They were assigned the anisotropic temperature factors of the atoms to which they are bonded. After refinement of the positions of all the atoms, $R = 0.053$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.068$ using Cruickshank's weighting scheme with $a = 5$, $c = 0.02$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). In the final cycles, 128 reflections which did not meet the condition $0.5 < |F_c|/|F_o| < 2.0$ were excluded. A final difference map showed a maximum peak of 0.4 e Å⁻³.

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974). The Patterson and electron density maps and the full-matrix least-squares refinement were computed with the *TLS* programs (Sklenář, 1973) and interatomic distances and bond angles with *ORFFE* (Busing, Martin & Levy, 1964) on an IBM 370/135 computer.

Results and discussion

The final atomic parameters are given in Table 1,* interatomic distances, bond angles and the symmetry code are in Table 2.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34001 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$; for H $\times 10^2$) with *e.s.d.*'s in parentheses

	x	y	z
Pd	0	0	0
Br	1068 (1)	1482 (1)	1061 (1)
P	422 (2)	-704 (1)	1812 (2)
O(1)	-3945 (7)	-816 (5)	1369 (6)
O(2)	-3263 (7)	-151 (4)	94 (6)
C(1)	-1424 (10)	-1283 (6)	1588 (9)
C(2)	-2962 (8)	-686 (5)	937 (7)
C(3)	1937 (9)	-1630 (6)	2324 (8)
C(4)	2899 (11)	-1716 (7)	1812 (9)
C(5)	4066 (12)	-2426 (8)	2183 (10)
C(6)	4243 (12)	-3029 (7)	3093 (11)
C(7)	3320 (13)	-2955 (8)	3640 (10)
C(8)	2122 (11)	-2260 (8)	3237 (10)
C(9)	1089 (10)	-1 (6)	3210 (8)
C(10)	9 (12)	502 (8)	3367 (10)
C(11)	511 (16)	1087 (10)	4398 (11)
C(12)	2096 (15)	1159 (9)	5275 (12)
C(13)	3125 (20)	704 (19)	5064 (19)
C(14)	2672 (16)	77 (16)	4095 (18)
H(1)	-16 (1)	-16 (1)	22 (1)
H(2)	-16 (1)	-18 (1)	10 (1)
H(3)	-48 (1)	-4 (1)	7 (1)
H(4)	26 (1)	-13 (1)	11 (1)
H(5)	47 (1)	-24 (1)	18 (1)
H(6)	50 (1)	-35 (1)	33 (1)
H(7)	34 (1)	-35 (1)	41 (1)
H(8)	14 (1)	-23 (1)	36 (1)
H(10)	-11 (1)	5 (1)	27 (1)
H(11)	-1 (2)	16 (1)	45 (1)
H(12)	23 (2)	17 (1)	58 (1)
H(13)	42 (2)	6 (2)	58 (2)
H(14)	34 (2)	0 (2)	38 (2)

Table 2. Interatomic distances (Å) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

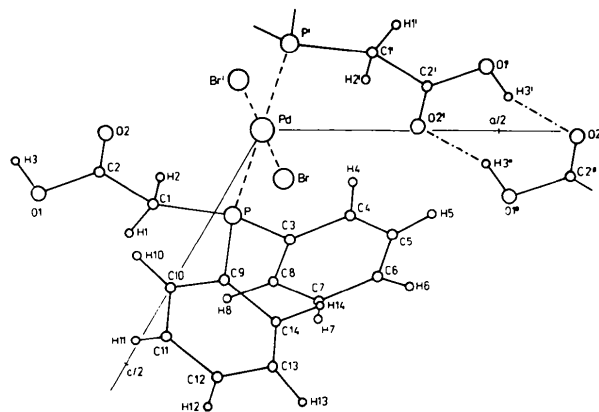
Symmetry code			
(i) $-x, -y, -z$	(ii) $1 + x, y, z$		
Pd—Br	2.447 (1)	Br—Pd—P	92.24 (5)
—P	2.322 (2)	Br—Pd—O(2)	100.4 (1)
—O(2)	3.171 (6)	P—Pd—O(2)	67.3 (1)
P—C(1)	1.831 (8)	Pd—P—C(1)	112.5 (2)
—C(3)	1.823 (8)	Pd—P—C(3)	111.9 (2)
—C(9)	1.829 (8)	Pd—P—C(9)	114.6 (2)
C(1)—C(2)	1.523 (11)	C(1)—P—C(3)	103.9 (4)
—H(1)	0.98 (11)	C(1)—P—C(9)	103.5 (4)
—H(2)	1.00 (11)	C(3)—P—C(9)	104.4 (4)
C(2)—O(1)	1.311 (9)	O(1 ⁱ)—H(3 ⁱ)—O(2 ⁱⁱ)	153 (11)
—O(2)	1.216 (9)		
O(1 ⁱ)—O(2 ⁱⁱ)	2.710 (7)		
—H(3 ⁱ)	1.01 (12)		
O(2 ⁱⁱ)—H(3 ⁱ)	1.77 (12)		

The Pd atom is hexacoordinate, as can be seen from the projection of the structure down *b* (Fig. 1). In the equatorial plane of the distorted coordination octahedron, two *trans* Br atoms and two *trans* P atoms form an almost regular square. The Pd—P and P—C

distances are similar to those in other palladium(II)-halide-phosphine complexes, *e.g.* dichlorobis(diphenylphosphine)ethylaminepalladium(II), Pd—P 2.224 (3), P—C 1.813 (20) Å (Payne, Mokuolo & Speakman, 1965). Similarly, the Pd—Br distance is similar to the analogous distances in bis(dimethyl sulphide)tetrabromodipalladium(II): Pd—Br (terminal) 2.404 (4), Pd—Br (bridging) 2.429 (4) and 2.447 (11) Å (Sales, Stokes & Woodward, 1968). In the axial positions, two carbonyl O atoms from ligand molecules complete the coordination to form a distorted octahedral environment with a Pd—O(2) distance of 3.171 (6) Å. A similar feature is assumed as non-bonding in the structure of PdCl₂·H₄EDTA·5H₂O (Robinson & Kennard, 1970).

The chains of molecules are connected by twofold hydrogen bonding of the COOH::HOOC type (according to the centre of symmetry) with distances O(1ⁱ)—H(3ⁱ) 1.01 (12), H(3ⁱ)···O(2ⁱⁱ) 1.77 (12), O(1ⁱ)···O(2ⁱⁱ) 2.710 (7) Å, O(1ⁱ)—H(3ⁱ)—O(2ⁱⁱ) 153 (11) $^\circ$. The planar COOH::HOOC moiety is similar to that of other carboxylic acids, *e.g.* benzoic acid (Sim, Robertson & Goodwin, 1955; O···O 2.64 Å), terephthalic acid (Bailey & Brown, 1967; O···O 2.62 Å) and adipic acid (Housty & Hospital, 1965; O···O 2.64 Å). Nevertheless, the significant lengthening of the O···O distance in the present study suggests a slight bonding interaction between the carbonyl O and Pd. The hydrogen bonding is also reflected in the infrared spectra; as for the simple carboxylic acids mentioned, the spectrum of the Pd complex is characterized by a broad band centred on 306.0 mm⁻¹ with a typical envelope originating from the C—H stretching.

The distances and angles in the ligand are normal and fall into the range typical for arylphosphine complexes {*e.g.* [CuBrPPh₃]₄·2CHCl₃; Churchill & Kalra, 1974}: the phenyl C—C distance is 1.313–1.403 Å and the phenyl C—C—C angle 116.0–124.9 $^\circ$.

Fig. 1. Projection of the structure down *b*.

The two phenyl groups are planar with the following coefficients of the plane equations (the phenyl-phenyl angle is 76°):

	C(3)–C(8) phenyl	C(9)–C(14) phenyl
A	1.118 ± 0.086	-1.147 ± 0.090
B	1.806 ± 0.138	-2.156 ± 0.165
C	2.102 ± 0.161	1.480 ± 0.114
D	-1.363 ± 0.108	-6.276 ± 0.485

The mean distances of the phenyl C atoms (distances in parentheses are for the P atom) from the plane are 0.01 (0.01 Å) for the first phenyl and 0.03 (0.11 Å) for the second phenyl.

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The Structure of a Complex between Rubidium Thiocyanate, Water and Dibenzo-[*b,q*][1,4,7,10,13,16,19,22,25,28]decaoxacyclotriacontane (Dibenzo-30-crown-10)

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(Received 15 June 1977; accepted 16 October 1978)

Abstract

The crystal and molecular structure of dibenzo-30-crown-10. $\text{RbSCN} \cdot \text{H}_2\text{O}$ [$\text{Rb}(\text{C}_{28}\text{H}_{40}\text{O}_{10})\text{SCN} \cdot \text{H}_2\text{O}$, $\text{C}_{28}\text{H}_{40}\text{O}_{10}\text{Rb}^+ \cdot \text{SCN}^- \cdot \text{H}_2\text{O}$] has been determined by the heavy-atom method and refined to $R_1 = 0.046$ for 3251 observed reflexions measured with a Syntex $P2_1$ diffractometer. The cell is monoclinic, space group $P2_1/c$, with $a = 13.596$ (3), $b = 12.411$ (3), $c = 21.869$ (7) Å, $\beta = 114.36$ (2)°, $V = 3362$ (2) Å³, $Z = 4$. The macroring surrounds the Rb^+ cation. The SCN^- anions and water molecules form infinite chains and have no direct contact with the Rb^+ atom.

Introduction

One of the characteristic features of macrocyclic polyethers exists in their ability to form complexes with various inorganic cations, bound by ion-dipole interactions with electronegative O atoms in the macroring.

The structure of the title compound has been studied as part of the systematic investigation of the proper-

ties of macrocyclic polyethers containing 1,4,7,10-, 13,16-hexaoxacyclooctadecane (18-crown-6) and 1,4,7,10,13,16,19,22,25,28-decaoxacyclotriacontane (30-crown-10) (Hašek & Huml, 1975, 1976, 1978; Hašek, Hlavatá & Huml, 1977; Hlavatá, Hašek & Huml, 1978).

Experimental

The crystals (white) were prepared by Petránek & Ryba (1974). The molecular formula was confirmed by elemental analysis. All measurements were performed at room temperature.

Crystal data

$\text{C}_{28}\text{H}_{40}\text{O}_{10}\text{Rb}^+ \cdot \text{SCN}^- \cdot \text{H}_2\text{O}$, monoclinic, $P2_1/c$, $a = 13.596$ (3), $b = 12.411$ (3), $c = 21.869$ (7) Å, $\beta = 114.36$ (2)°, $V = 3362$ (2) Å³, $Z = 4$, $D_c = 1.38$, $D_m = 1.37$ Mg m⁻³ (flotation in heptane- CCl_4 solution), FW 680.1, m.p. 393–394 K, $F(000) = 1456$, $\mu(\text{Cu } K\alpha) = 3.28$ mm⁻¹.