CRYSTAL STRUCTURE OF BIS(ETHYLENEDIPHOSPHINETETRAACETIC ACID)PALLADIUM(II) BIS(DIHYDROGENETHYLENEDIPHOSPHINETETRAACETATO)PALLADATE(II) TETRAHYDRATE HYDROBROMIDE (1/1): AN UNUSUAL CASE OF BROMIDE UNCOORDINATED TO PALLADIUM(II)

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Synthesis, crystal and molecular structure of the title compound as a representative of the complexes of phosphineacetic acids with soft metal ions is described. Crystal data: triclinic, $P\bar{1}$, a = 10.809(1), b = 14.922(1), c = 10.617(1) Å, α = 108.871(7), β = 102.773(9), γ = 102.970(7) °, Z = 1, R = 0.031 for 4 545 observed reflections. The structure is built of layers composed of hydrogen-bonded ligands; the layers are joined, in alternate manner, by Pd(II) ions, water molecules and bromide anions. As an average, one proton of the tetraprotonated ligand is released during complexation even in protic solvent (aqueous acetic acid), resulting in the given ionic composition with non-equivalent Pd(II) centers. The carboxyl groups and, surprisingly, even the bromide ion are not coordinated to Pd. The proton assigned formally to hydrobromic acid was not located and is possibly disordered.

As a consequence of different steric and/or electronic properties of phosphorus compared with nitrogen, the coordination behaviour of ethylenediphoshinetetraacetic acid (H_4L) appears to be remarkably different from its nitrogen analogue, the familiar EDTA. While the crystal structure[1] of the completely protonated ligand, H_4L . 2 HBr, is completely analogous to H_4EDTA . 2 HCl, the structures of both metal complexes of L^{4-} determined till now do not exhibit any similarity to their EDTA counterparts. In the mixed Ni(II)/Mn(II) complex of the Mn_3NiL_2 . 16 H_2O composition[2], the L^{4-} anions act as P,P-chelating to a distorted square planar Ni(II) ion and simultaneously as multiply O-bridging to octahedral Mn(II) ions. In contrast, the structure of Cd_2L . 6 H_2O is built of irregular CdO_6P polyhedra linked by μ-hexadentate ligand anions[3]. Clearly, the presence of carboxylate groups supports the formation of polymeric COO-bridged structures. It appeared therefore interesting to look for a compound containing protonated ligand in which the bridging function of carboxyl groups should be at least partially blocked. The palladium(II) complex described in this paper seems to fulfill these needs.

EXPERIMENTAL

Synthesis of the complex. Hydrated palladium(II) bromide (36 mg, 0.1 mmol) and H_4L . 2 HBr (ref.[1], 98 mg, 0.2 mmol) were dissolved in 90% acetic acid by gentle warming to give a colorless solution. Vacuum evaporation provided an impure pale yellow material which was repeatedly crystallized from 90% acetic acid. Washing with a little cold acetic acid, then with acetone and drying in air at room temperature gave 53 mg (63%) of the product as colorless needles of X-ray quality which appear to be unlimitedly stable in air. For $[Pd(H_4L)_2][Pd(H_2L)_2]$. 4 H_2O . HBr ($C_{40}H_{69}BrO_{36}P_8Pd_2$, m.w. 1 666.5) calculated: 28.83% C, 4.17% H, 4.80% Br; found: 28.77% C, 4.21% H, 4.86% Br; IR (Nujol) 1 586 m (COO^-), 1 676 s (COOH), 3 380 m, vb (H_2O); m.p. 225 – 227 °C (dec.).

Crystallography. Triclinic, a = 10.809(1), b = 14.922(1), c = 10.617(1) Å, α = 108.871(7), β = 102.773(9), γ = 102.970(7)°, Z = 1, V = 1 496.8(4) Å (by least-squares refinement on diffractometer angles for 23 automatically centered reflections, λ = 0.71073 Å), space group $P\bar{1}$ (No. 2), ρ_m = 1.84, ρ_C = 1.858 g cm^{-3}, $F(000)$ = 844. Crystal dimensions 0.10 × 0.15 × 0.35 mm, $\mu(MoK\alpha)$ = 15.5 cm^{-1}. CAD4 diffractometer, graphite-monochromated MoKα radiation, $\omega/2\theta$ scan, 8 235 reflections measured ($0 \le 2\theta \le 52°$, $-13 \le h \le 13$, $-14 \le k \le 14$, $-13 \le l \le 13$), 5 013 unique (no absorption correction) giving 4 545 with $I > 1.96\ \sigma(I)$. Two standard reflections monitored every 2 h showed no significant intensity fluctuation.

The structure was solved by the heavy atom metod (SHELXS86, ref.[4]) yielding the positions of Pd and Br atoms, and then developed by consecutive Fourier series providing the positions of all non-hydrogen atoms. After a series of least-squares refinements (SHELX76, ref.[5]), the difference electron density map enabled location of all hydrogen atoms except the (formal) half-proton required for electroneutrality of the formula unit. In order to satisfy the centrosymmetric space group which was clearly indicated by the E^2-1 statistics, this proton should be located at the inversion centre; no signs of any significant electron density at the possible places (with respect to O–O contacts) could be found in the difference map, however. The structure was eventually refined by full-matrix least-squares in the $P\bar{1}$ space group for the reasons discussed later. As the hydrogen atoms proved to be unstable towards free refinement, they were fixed either in theoretical positions (hydrogens of the methylene groups) or in the positions found from the difference map (all other hydrogens) and assigned individual group temperature factors for methylene, carboxylic and water hydrogens, respectively. The refinement converged at R = 0.031, wR = 0.036 [$w = (\sigma^2(F) + 0.0009\ F^2)^{-1}$] for 4 545 observed reflections. The final difference map showed no peaks of chemical significance. Tables I and II summarize the atomic position parameters, bond lengths and angles. Tables of structure factors, hydrogen atom coordinates and anisotropic temperature factors of non-H atoms are available from the authors upon request.

RESULTS AND DISCUSSION

The structure (Figs 1, 2) is arranged into chains of hydrogen-bonded carboxyphosphine ligands running parallel to the crystallographic *bc*-plane and linked along the *b*-axis by coordinated Pd(II) ions and hydrogen-bonded water molecules in alternating manner. There are further hydrogen bonds with imposed crystallographic symmetry between the bromide ions and COOH groups which join the chains in the *a*-direction. In terms of coordination chemistry, linking of the chains by palladium(II) results in two structurally different $Pd(H_nL)_2$ moieties in which the Pd(II) ions are chelated by two PCH_2CH_2P groups, resulting in a distorted square planar arrangement. The PdP_4 moieties are implicitly planar due to crystallographic symmetry; the distorsion of bond

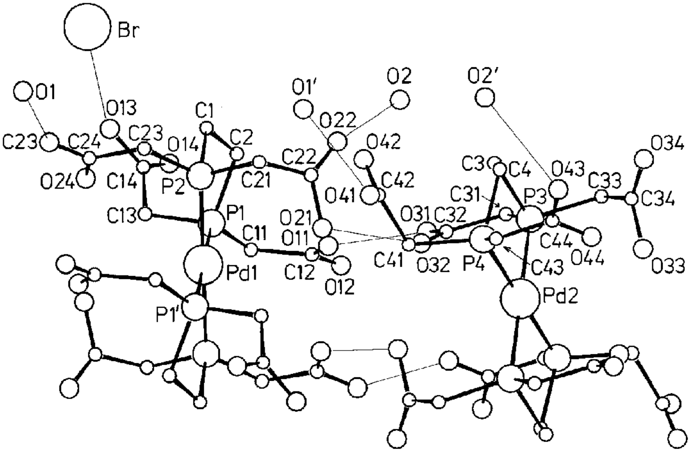

FIG. 1
Perspective view of the formula unit with hydrogen bonds depicted as thin lines

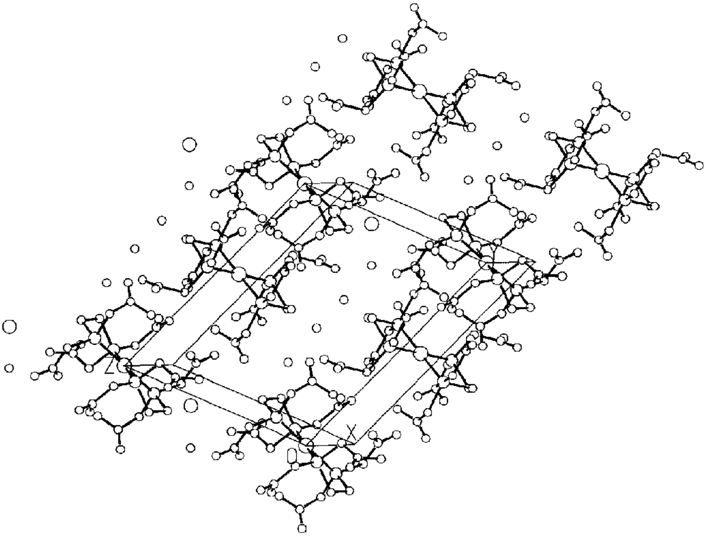

FIG. 2
Crystal packing scheme

TABLE I
Fractional coordinates (. 10^4) and equivalent isotropic thermal parameters (. 10^3) of non-hydrogen atoms with estimated standard deviations (e.s.d.'s) in parentheses

$$U_{eq} = (U_{11} + U_{22} + U_{33} + 2U_{12} \cos \alpha + 2U_{13} \cos \beta + 2U_{23} \cos \gamma)/3$$

Atom	x	y	z	U_{eq}, Å^2
Pd1	0	0	0	16.1(1)
Pd2	5000	5000	0	17.6(1)
Br	5000	0	5000	61.2(3)
P1	−1659(1)	580(1)	730(1)	20.6(2)
P2	1012(1)	479(1)	2387(1)	21.1(2)
P3	4272(1)	5788(1)	1839(1)	22.3(2)
P4	6331(1)	4637(1)	1719(1)	22.9(2)
O1	2874(4)	−2268(3)	4860(4)	80(2)
O2	931(6)	4578(4)	4211(6)	138(3)
O11	−599(2)	2419(2)	339(3)	50(1)
O12	−2490(3)	2672(2)	−497(3)	47(1)
O13	−3511(4)	−430(3)	2750(4)	72(2)
O14	−4358(3)	466(2)	1717(3)	43(1)
O21	2284(3)	2192(2)	1307(2)	33(1)
O22	2186(3)	3063(2)	3419(3)	47(1)
O23	623(3)	−1961(2)	3176(3)	55(1)
O24	−829(2)	−1433(2)	2013(3)	41(1)
O31	518(3)	4186(2)	869(4)	55(1)
O32	2422(2)	3843(2)	929(3)	36(1)
O33	6673(2)	7386(2)	1519(2)	36(1)
O34	7256(3)	7971(2)	3838(3)	48(1)
O41	6952(4)	2873(3)	2970(4)	68(1)
O42	5208(3)	3151(3)	3522(3)	68(1)
O43	10097(4)	6001(3)	3631(4)	99(2)
O44	8770(3)	6373(2)	2208(4)	70(1)
C1	−894(3)	1450(3)	2575(3)	30(1)
C2	−30(3)	1007(3)	3379(3)	30(1)
C3	4918(4)	5485(3)	3341(3)	33(1)
C4	6308(4)	5417(3)	3439(3)	31(1)
C11	−2645(3)	1190(2)	−121(4)	28(1)
C12	−1873(3)	2178(3)	−112(4)	29(1)
C13	−2980(3)	−437(2)	730(3)	25(1)
C14	−3706(3)	−83(3)	1752(4)	29(1)
C21	2604(3)	1498(2)	3003(3)	27(1)
C22	2361(3)	2350(2)	2626(4)	29(1)
C23	1463(3)	−380(3)	3152(4)	30(1)
C24	303(3)	−1327(3)	2714(4)	31(1)

TABLE I
(*Continued*)

Atom	*x*	*y*	*z*	U_{eq}, Å^2
C31	2493(3)	5544(2)	1639(4)	30(1)
C32	1761(4)	4427(3)	1089(4)	33(1)
C33	4934(3)	7162(2)	2514(4)	31(1)
C34	6418(3)	7552(2)	2723(3)	28(1)
C41	5521(3)	3341(3)	1461(3)	29(1)
C42	5865(4)	3114(3)	2768(4)	42(1)
C43	8085(3)	4718(3)	2047(4)	34(1)
C44	9049(3)	5765(3)	2666(4)	34(1)

angles at Pd(II) originates from steric requirements of the five-membered chelate rings. Notably, the conformation of the chelate ring at Pd1 differs from that at Pd2: while the ring at Pd2 adopts an approximate C_2 symmetry (half-chair, C_2-axis through Pd) which is usual for the $MPCH_2CH_2P$ moiety[6], that on Pd1 is close to the C_S envelope with mirror plane passing through the C-atom; the paucity of comparable data prevents to judge whether this is the result of hydrogen bonding or crystal packing or both.

The carboxyl groups (partly protonated), water molecules and bromide anions are not coordinated to Pd(II) being involved, instead, in a system of hydrogen bonds which are summarized in Table III. While the bond distances and angles at the phosphorus atoms and within the acetate groups are normal and require no comment, the intra- and inter-chain hydrogen bonding leads to remarkably different conformation of the acetate substituents on the palladium centers (see Fig. 3 where the two $Pd(H_nL)_2$ moieties are superimposed).

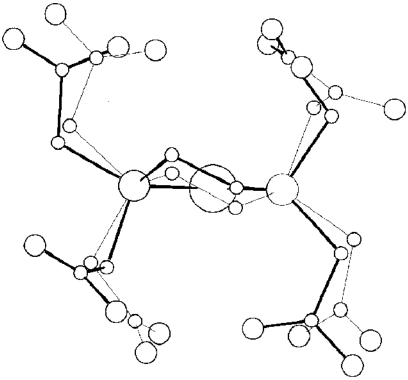

FIG. 3
Superposition of the crystallographically independent parts bonded to Pd1 (solid lines) and Pd2 with PdP_2 units taken as the reference

TABLE II
Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Atoms	Distances	Atoms	Distances
Pd1–P1	2.333(1)	O22–C22	1.207(5)
Pd1–P2	2.320(1)	O23–C24	1.276(5)
Pd2–P3	2.329(1)	O24–C24	1.229(4)
Pd2–P4	2.350(1)	O31–C32	1.257(6)
P1–C1	1.834(3)	O32–C32	1.239(5)
P1–C11	1.823(4)	O33–C34	1.324(4)
P1–C13	1.836(4)	O34–C34	1.186(4)
P2–C2	1.840(4)	O41–C42	1.298(6)
P2–C21	1.840(3)	O42–C42	1.178(5)
P2–C23	1.822(5)	O43–C44	1.237(6)
P3–C3	1.831(4)	O44–C44	1.222(6)
P3–C31	1.825(4)	C1–C2	1.526(5)
P3–C33	1.842(4)	C3–C4	1.511(6)
P4–C4	1.830(3)	C11–C12	1.518(6)
P4–C41	1.837(5)	C13–C14	1.505(5)
P4–C43	1.819(4)	C21–C22	1.509(5)
O11–C12	1.277(4)	C23–C24	1.519(6)
O12–C12	1.204(5)	C31–C32	1.523(6)
O13–C14	1.319(6)	C33–C34	1.517(5)
O14–C14	1.199(5)	C41–C42	1.520(5)
O21–C22	1.323(4)	C43–C44	1.504(6)

Atoms	Angles	Atoms	Angles
P2–Pd1–P1	83.4(1)	O12–C12–O11	125.6(4)
P4–Pd2–P3	83.0(1)	C11–C12–O11	115.7(3)
C1–P1–Pd1	107.4(1)	C11–C12–O12	118.7(3)
C11–P1–Pd1	124.7(1)	C14–C13–P1	113.4(2)
C13–P1–Pd1	111.1(1)	O14–C14–O13	122.6(3)
C11–P1–C1	105.6(2)	C13–C14–O13	111.5(3)
C13–P1–C1	105.0(2)	C13–C14–O14	125.8(3)
C13–P1–C11	101.4(2)	C22–C21–P2	109.7(2)
C2–P2–Pd1	110.2(1)	O22–C22–O21	124.4(3)
C21–P2–Pd1	110.0(1)	C21–C22–O21	112.0(3)
C23–P2–Pd1	123.1(1)	C21–C22–O22	123.5(3)
C21–P2–C2	105.3(2)	C24–C23–P2	112.7(3)
C23–P2–C2	103.7(2)	O24–C24–O23	125.0(3)
C23–P2–C21	103.1(2)	C23–C24–O23	113.5(3)

TABLE II
(*Continued*)

Atoms	Angles	Atoms	Angles
C3–P3–Pd2	109.5(1)	C23–C24–O24	121.5(3)
C31–P3–Pd2	121.4(1)	C32–C31–P3	111.1(2)
C33–P3–Pd2	112.9(1)	O32–C32–O31	125.8(4)
C31–P3–C3	103.6(2)	C31–C32–O31	115.5(3)
C33–P3–C3	104.6(2)	C31–C32–O32	118.7(3)
C33–P3–C31	103.2(2)	C34–C33–P3	113.1(2)
C4–P4–Pd2	108.3(1)	O34–C34–O33	123.6(3)
C41–P4–Pd2	108.1(1)	C33–C34–O33	112.4(2)
C43–P4–Pd2	127.5(1)	C33–C34–O34	123.9(3)
C41–P4–C4	105.8(2)	C42–C41–P4	114.9(2)
C43–P4–C4	102.7(2)	O42–C42–O41	123.3(4)
C43–P4–C41	102.6(2)	C41–C42–O41	113.4(3)
C2–C1–P1	109.6(2)	C41–C42–O42	123.3(3)
C1–C2–P2	110.9(2)	C44–C43–P4	114.7(3)
C4–C3–P3	110.1(2)	O44–C44–O43	121.1(4)
C3–C4–P4	110.0(2)	C43–C44–O43	120.0(4)
C12–C11–P1	116.2(2)	C43–C44–O44	118.8(3)

TABLE III
Hydrogen bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Atom X	Atom H	Atom Y	Distance			Angle X–H–Y
			X...Y	X–H	Y...H	
O1	HO1A	O23	2.904(5)	1.0	1.9	173
O2	HO2A	O22	2.883(7)	1.1	1.8	176
O2	HO2B	$O43^{i}$	2.678(8)	1.1	1.7	150
O11	HO11	O31	2.457(5)	1.3	1.2	173
$O13^{ii}$	$HO13^{ii}$	Br	3.143(4)	1.1	2.1	155
O21	HO21	O32	2.599(4)	1.0	1.7	169
O23	HO23	$O44^{i}$	2.540(5)	0.9	1.6	171
O33	HO33	$O24^{iii}$	2.704(4)	0.9	1.8	150
O41	HO41	$O1^{iv}$	2.718(6)	1.1	1.7	163

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

In carboxylate structures, hydrogen bonding usually acts as a strong averaging factor of carboxylate groups geometry, making sometimes difficult to differentiate between protonated and dissociated carboxyls. With regard to the inherently limited precision of the O–H distances determined by X-ray diffraction (ca 0.1 Å), an additional criterion for distinguishing between dissociated and protonated carboxyl groups, e.g. these based on their overall geometry is necessary. Using the criterion of Borthwick[7] and taking into account the H-atom positions which are unambiguous, there are undoubtedly one COO (C43) and five COOH groups (C13, C21, C23, C33, C41) from the total of eight in the asymmetric unit of the present structure. As regards the remaining two carboxyl groups, that on C11 forms a very short intrachain hydrogen bond to the C31 carboxyl. The hydrogen atom of this bond lies, within the estimated error of the O–H bond length, in the midpoint of the O11–O31 distance; the geometry of the two carboxyl groups involved, however, unambiguously classifies the C31 carboxyl as dissociated and hence the C11 carboxyl as protonated.

In summary, the chemical formula of the complex is best formulated as $[Pd(H_4L)_2]^{2+}[Pd(H_2L)_2]^{2-} \cdot 4\,H_2O \cdot HBr$, thus explaining nicely the crystallographic inequivalence of the Pd atoms reflecting, e.g., in different conformations of chelate rings and slightly but significantly differing Pd–P bond lengths. The question remains, however, about the location of the proton formally assigned to the "HBr molecule of solvation". Unfortunately, this proton (a half of proton in terms of the asymmetric unit) could not be located on the basis of the data, despite extensive searching of difference maps calculated in the non-centrosymmetric *P1* space group. The anomalously high temperature factors of two oxygen atoms (O2 and O43) seem to indicate that the elusive proton might be located between O2 and O43, possibly as a disordered H_2O/H_3O^+ system at O2, a situation which is not uncommon in related structures[8,9].

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